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CHEMICAL & ATMOSPHERIC SCIENCES

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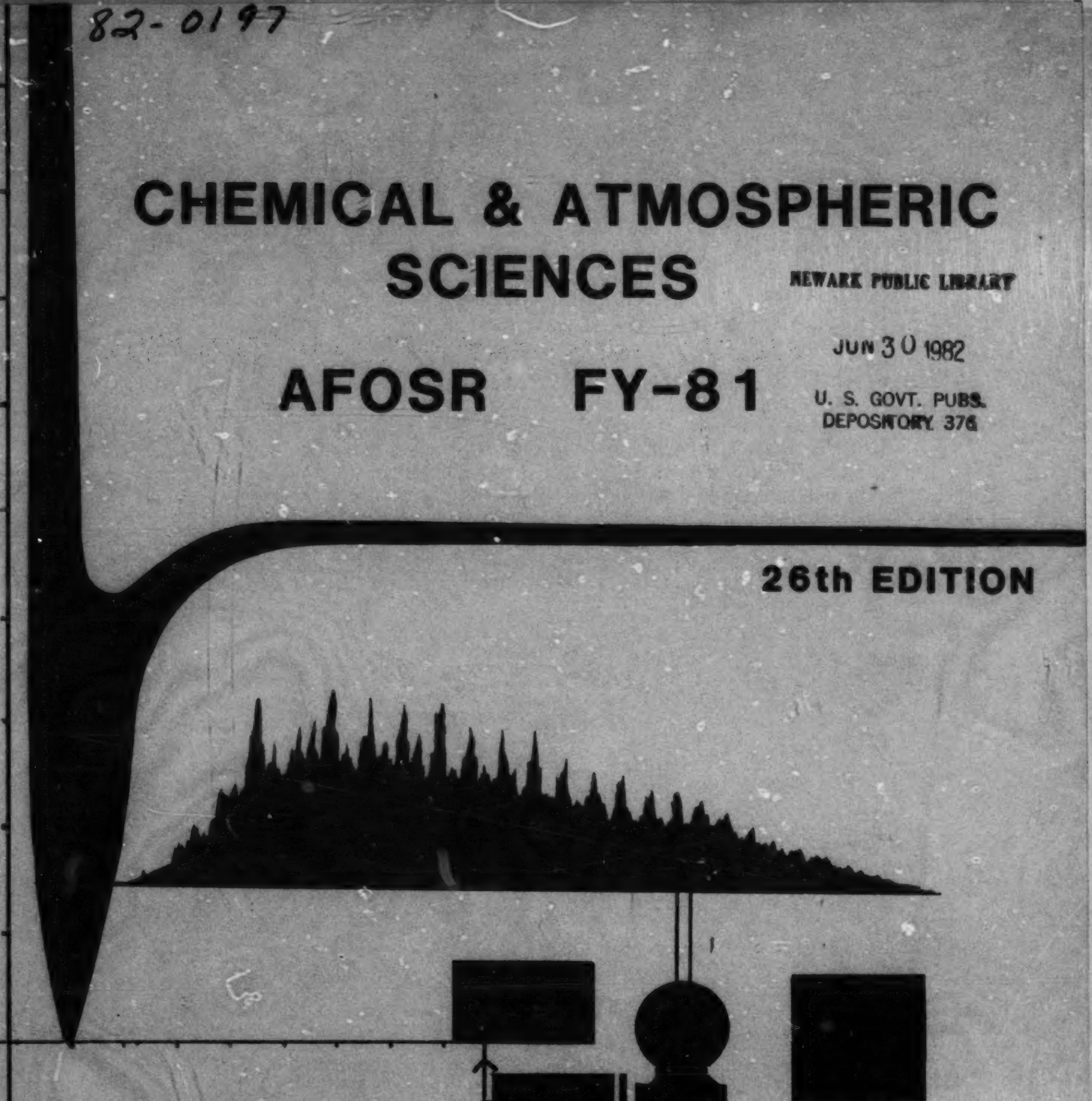

26th EDITION

Air Force Office
of Scientific Research
Air Force Systems Command
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COVER

The cover is an artistic representation of some results from the laboratory of the late Dr. Michael A. A. Clyne at Queen Mary College, England. Each of the figures represents elements of modern spectroscopy: an apparatus for obtaining and resolving chemiluminescent and fluorescent emissions, a chemiluminescence spectrum, and a potential curve of the interaction of two atoms forming a diatomic molecule which can be obtained from an analysis of such spectra. A thorough characterization of the spectroscopy and "quantum dynamics" of molecular species such as the interhalogens is leading to new potential chemical lasers.

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Cloud Physics
Mesoscale Weather Forecasting
Radar Atmospheric Research
Meteorology
Upper Atmosphere

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A review is presented of research efforts sponsored by the Directorate of Chemical and Atmospheric Sciences which have completed their period of support. Illustrated accounts resulting from the basic research programs in the Atmospheric and Chemical Sciences are highlighted. The Atmospheric Sciences is concerned with meteorology and upper atmospheric structure and dynamics. The meteorology focuses on mesoscale meteorology, cloud physics, and atmospheric dynamics. The Chemical Sciences deal with Chemical Techniques, Chemical Structures, Surface Chemistry, Chemical Dynamics, and Synthesis and properties of Materials.

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26TH AFOSR
CHEMICAL & ATMOSPHERIC SCIENCES
PROGRAM REVIEW

FY81

WILLIAM G. THORPE & LEE E. MYERS, EDITORS
SYLVIA A. STALLINGS, MANAGING EDITOR

MARCH 1982

AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
DIRECTORATE OF CHEMICAL AND ATMOSPHERIC SCIENCES
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WASHINGTON, D. C. 20332

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Dr. Donald R. Ulrich 59

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Research in Fluorochemical Synthesis
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Atmospheric Sciences
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MISSION

The Directorate of Chemical and Atmospheric Sciences of the Air Force Office of Scientific Research has the mission to encourage and support fundamental research designed to increase knowledge and understanding to stimulate the recognition of new concepts, and to provide for early exploitation of their military implications.

The Directorate obtains and maintains for the Air Force a diversified program of research at in-house laboratories as well as extramurally at university and industrial laboratories. The Directorate also functions as a dynamic interface between the Air Force and the scientific community, ensuring the free, full, and constant interchange of ideas from each to the other through publications, personal contacts, meeting attendance, and sponsored symposia. In these ways, the Directorate helps the Air Force maintain technological superiority.

TECHNICAL STAFF

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Capt Lee E. Myers
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Lt Col Ted S. Cress
Program Manager
Atmospheric Sciences

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DEPARTMENT OF THE AIR FORCE
AIR FORCE OFFICE OF SCIENTIFIC RESEARCH (AFSC)
BOLLING AIR FORCE BASE, DC 20332

March 1982

TO: FRIENDS OF AFOSR

The content of this review combines highlights from the past, together with forecasts of future emphasis. Collectively it is intended to facilitate acquaintanceship by the technical community on just what we consider most significant. With planned distribution of 1500 copies of this edition we continue a Directorate tradition that began thirty years ago.

You will find a postal reply card inclosed with your copy. It is important that you return this card to us with indication of whether you wish to continue to be on our mailing list. Naturally, we want to target the mailing to only those who are interested. Also, we want to improve future editions based on your constructive criticism.

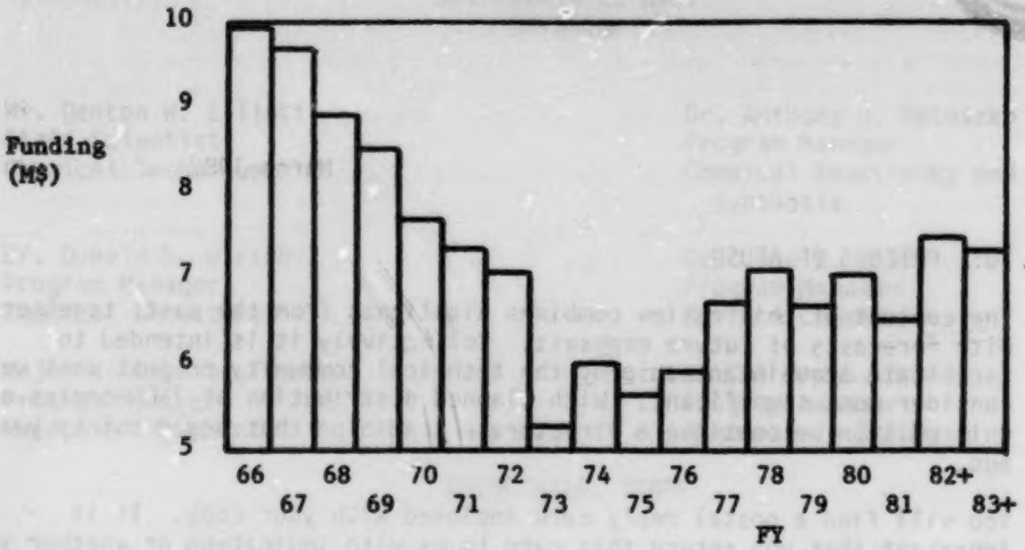
Sincerely

Donald L Ball

DONALD L. BALL
Director of Chemical &
Atmospheric Sciences

Recent Chemistry Funding

1982 Dollars*



*** 1982 basis year**

+ projected budget and inflation

- -

FY81 CHEMISTRY PROGRAM STATISTICS

Total number of proposals received	**272**
Total number of inquiries received	**194**
New work efforts initiated	**43**
Renewals	**71**
Proposals declined	**108**
Proposals withdrawn	**12**
Proposals transferred	**12**
Mini-Grants (one year funding)	**5**
Conferences and Symposia	**7**

CONFERENCES AND SYMPOSIA

The following conferences and symposia were held during FY 81 with funds provided in part or wholly by the Directorate of Chemical and Atmospheric Sciences as a means of furthering areas of scientific research of particular interest to the Air Force.

1981 Gordon Research Conference on Electrochemistry

Dr. Stephen W. Feldberg
Ventura, California
25-30 January 1981

DOD/NASA Workshop on Structural Adhesives Research

Dr. W. Click
University of Dayton
Dayton, Ohio
23-24 April 1981

Third Symposium on Applied Surface Analysis

Dr. John T. Grant
University of Dayton
Dayton, Ohio
3-5 June 1981

1981 Gordon Research Conference on
Molecular Energy Transfer

Dr. Thomas F. George
Brewster Academy
Wolfeboro, New Hampshire
29 June - 3 July 1981

Sixth Conference on Glass Science in Glass
Microstructure-Surface and Bulk

Dr. Guy E. Rindone
Pennsylvania State University
University Park, Pennsylvania
29-31 July 1981

Gordon Research Conference on Glass

Dr. P. Schultz
Plymouth, New Hampshire
3-7 August 1981

The Fifth International Summer Institute in Surface Science

Dr. Ralf Vansilow
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin
24-28 August 1981

ACTIVE RESEARCH EFFORTS

CHEMISTRY

As of 1 Oct 1981

Alphabetical by Principal Investigator

Distibines, New One-Dimensional Materials (AJM) AFOSR-81-0099, 2303/B2	Arthur J. Ashe, III Department of Chemistry University of Michigan Ann Arbor, MI 48109
Transport Properties and Structure of Extended-Chain Polymers (DRU) AFOSR-80-0014, 2303/A3	R. Edward Barker, Jr. Kenneth R. Lawless Department of Materials Science University of Virginia Charlottesville, VA 22901
Rates of Intramolecular Conversions Over Low Barriers (WGT) AFOSR-80-0046, 2303/B1	Simon Bauer Department of Chemistry Cornell University Ithaca, New York 14853
New Approaches to the Synthesis of Novel Organosilanes (AJM) AFOSR-80-0239, 2303/B2	Philip Boudjouk Department of Chemistry North Dakota State University Fargo, North Dakota 58105
Underpotential Metal Deposition and Trace Analysis Using Solid Electrodes (DWE) AFOSR-78-3621, 2303/A1	Stanley Bruckenstein Department of Chemistry State University of New York Buffalo, New York 14214
Molten Salt Electrochemical System (DWE) AFOSR-80-0173, 2303/A1	Roger K. Bunting Department of Chemistry Illinois State University Normal-Bloomington, IL 61761
Study in Molecular Lasers (WGT) AFOSR-81-0028, 2303/B1	George Burns Department of Chemistry University of Toronto Toronto, Ontario, Canada M5S 1A1

New Approaches to Functionalized Fluorocarbons (AJM) AFOSR-80-0259, 2303/B2	D. Burton Department of Chemistry University of Iowa Iowa City, IA 52242
The Chemistry of Antioxidant in Solid Rocket Propellants (AJM) AFOSR-81-0095, 2303/D9	J. Chiang Chemistry Department State University of New York Oneonta, NY 13820
Chemical Kinetic Studies Involving NF and PF Radicals (WGT) AFOSR-78-3507, 2303/B1	M. A. A. Clyne (now deceased) Department of Chemistry Queen Mary College London E1 4NS, England
Ion Photofragment Spectroscopy: Structure and Dissociation of Molecular Ion (WGT) F49620-81-K-0006, 2303/B1	Philip C. Cosby James R. Peterson Molecular Physics Laboratory SRI International Menlo Park, CA 94025
Structural Electronic Relationships in Polymeric Solids (DRU) AFOSR-80-0038, 2303/A3	Glenn A. Crosby Department of Chemistry Washington State University Pullman, Washington 99164
Theoretical Studies of Metal Oxides (WGT) AFOSR-78-3677, 2303/B1	Alex Dalgarno K. Kirby Harvard College Observatory Cambridge, MA 02138
Chemiluminescence and Laser Induced Fluorescence of Boron Atom Reactions (WGT) AFOSR-80-0061, 2303/B1	Paul Davidovits Department of Chemistry Boston College Chestnut Hill, MA 02167
Electrosorption of Organic Molecules (DWE) AFOSR-80-0262, 2303/A1	Robert de Levie Department of Chemistry Georgetown University Washington, D.C. 20057
New Laser Dye Systems Based on Luminescent Transition Metal Complexes (AJM) AFOSR-78-3590, 2303/B2	James N. Demas Department of Chemistry University of Virginia Charlottesville, VA 22901

Development of Practical MO Techniques for Prediction of the Properties and Behavior of Materials (AJM) AFOSR-79-0008, 2303/B2	Michael J. S. Dewar Department of Chemistry University of Texas Austin, Texas 78712
Evaluation of Chemical and Atmospheric Sciences Research Relevant to Current and Projected U.S. Air Force Interests (DWE) F49620-81-C-0085, 2303/A1	Joseph E. Earley Department of Chemistry Georgetown University Washington, D.C. 20057
Picosecond Laser Studies of Excited State Proton and Electron Transfer Phenomena (AJM) AFOSR-81-0009, 2303/B2	Kenneth B. Eisenthal Department of Chemistry Columbia University New York, New York 10027
High Resolution Electron Energy Loss Studies of Chemisorbed Species on Aluminum and Titanium (LEM) AFOSR-80-0154, 2303/A2	James L. Erskine John M. White Department of Physics University of Texas Austin, Texas 78712
Collisional Energy Exchange in Polyatomic Molecules (WGT) F49620-80-C-0026, 2303/B1	John B. Fenn Department of Engineering and Applied Science Yale University New Haven, Connecticut 06520
Sequential Excitation Preparation of Molecular Energy Levels with Special Structural and Chemical Properties (WGT) AFOSR 80-0254, 2303/B1	Robert W. Field James L. Kinsey Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
Physical and Morphological Properties of Polymers (DRU) AFOSR-82-0009, 2303/A3	Paul J. Flory Department of Chemistry Stanford University Stanford, California 94305
Theoretical Studies of Laser-Induced Molecular Rate Processes: Topics in Line Broadening and Spectroscopy (WGT) F49520-78-C-0005, 2303/B1	Thomas F. George Department of Chemistry University of Rochester Rochester, New York 14627

Exploratory High Pressure Chemistry (AJM) AFOSR-79-0092, 2303/B2	John A. Gladysz Department of Chemistry University of California Los Angeles, California 90024
Spectroscopic Studies of the Products of the Reactions of Noble-Gas Atoms (WGT) AFOSR-79-0089, 2303/B1	Michael F. Golde Department of Chemistry University of Pittsburgh Pittsburgh, PA 15260
Multiphoton Dynamics: Energy Disposal During Decomposition of Molecules (WGT) F49620-78-C-0107, 2303/B1	David M. Golden John R. Barker Physical Sciences Division SRI International Menlo Park, California 94025
New Materials for Electrochemical Cells (DWE) AFOSR-77-3402, 2303/A1	John B. Goodenough Peter G. Dickens Inorganic Chemistry Laboratory Oxford University Oxford, OX1 3QR, England
Ultrastructure Processing and Environmental Stability of Advanced Structural and Electronic Materials (DRU) F49620-80-C-0047, 2303/A3	Larry L. Hench Department of Materials Science University of Florida Gainesville, Florida 32611
Theoretical Study of the Energetics and Dynamics of High Energy Inelastic Collision Processes (WGT) F49620-80-C-0017, 2303/B1	D. R. Herschbach Department of Chemistry Harvard University Cambridge, MA 02138
Laboratory Studies of Solvated Gas-Phase Anions (WGT) AFOSR-81-0105, 2303/D9	Peter M. Hierl Department of Chemistry University of Kansas Lawrence, KS 66045
Rotational Relaxation Studies of Hydrogen Fluoride (WGT) F496200-81-C-0011, 2303/B1	J. Hinchen Energy Research Laboratory United Technologies Research Center East Hartford, CT 06108
Energy Disposal in Electronically Excited Halogen Atoms and Molecular Oxygen (WGT) AFOSR-78-3513, 2303/B1	Paul L. Houston Department of Chemistry Cornell University Ithaca, New York 14853

Synthesis Structure and Reactivity of Molecules Attached to Electrode Surfaces (DWE) AFOSR-81-0149, 2303/A1	Arthur T. Hubbard Department of Chemistry University of California, Santa Barbara Santa Barbara, CA 93106
Synthesis and Characterization of Transition Metal Complex Systems with Novel Solid State Properties (AJM) F49620-79-C-0051, 2303/B2	L. V. Interrante Corporate Research and Development General Electric Company Schenectady, New York 12301
Molecular Order and Solidification Processes in Organic Liquids and Solutions (LEM) AFOSR-80-0166, 2303/A2	R. J. Jacobsen E. J. Drauglis Battelle Memorial Institute Columbus Laboratories 505 King Avenue Columbus, Ohio 43201
NMR Study of Disordered Materials under Extreme Conditions of Pressure and Temperature (DRU) AFOSR-81-0010, 2303/A3	Jiri Jonas Department of Chemistry University of Illinois Urbana, Illinois 61801
Structural and Synthetic Organosilicon Chemistry (AJM) AFOSR-81-0185, 2303/B2	Michael E. Jung Department of Chemistry University of California, Los Angeles Los Angeles, CA 90024
Effect of Structure on Physical Properties of Polymers (DRU) AFOSR-80-0101, 2303/A3	Frank E. Karasz Polymer Science & Engineering University of Massachusetts Amherst, Massachusetts 01003
Measurement of Rate Constants of Elementary Gas Reactions of Importance to Upper Atmosphere and Combustion Systems (WGT) AFOSR-80-0207, 2303/B1	Frederick Kaufmann Department of Chemistry University of Pittsburgh Pittsburgh, Pennsylvania 15260
Computer Modeling of Pulsed Chemical Lasers (WGT) AFOSR-80-0003, 2303/B1	Ronald L. Kerber Electrical & Mechanical Engineering Department Michigan State University East Lansing, Michigan 48824

Polyphosphorus Compounds Containing Phosphorus-Nitrogen Bonds (AJM) AFOSR-81-0051, 2303/B2	R. Bruce King Chemistry Department University of Georgia Athens, Georgia 30602
Spectroscopic Determination of Intermolecular Potentials of Gas Laser Components and of Major Atmospheric Constituents (WGT) AFOSR-77-3269, 2303/B1	William Klemperer Department of Chemistry Harvard University Cambridge, MA 02138
Time-Temperature Studies of High Temperature Deterioration Phenomena in Lubricant Systems: Synthetic Ester Lubricants (LEM) F49620-80-C-0061, 2303/A2	S. Koreck Fuel and Lubricants Department Ford Motor Company Dearborn, Michigan 48121
An Approach to Molecular Composites (DRU)(AJM) AFOSR-79-0080, 2303/A3 & 2303/B2	William R. Krigbaum J. Preston Department of Chemistry Duke University Durham, North Carolina 27706
The Quantum Dynamics of Chemical Reactions (WGT) AFOSR-81-0235, 2303/B1	Aron Kuppermann Division of Chemistry and Chemical Engineering California Institute of Technology Pasadena, California 91125
Electrocatalysis of Oxygen Using Water Soluble Metal Porphrins and Chemically Modified Porphyrin Electrodes (DWE) AFOSR-78-3672, 2303/A1	Theodore Kuwana Department of Chemistry Ohio State University Columbus, OH 43212
Studies of Polymer-Bound Macrocyclic Polytertiary Phosphines (AJM) AFOSR-79-0090, 2303/B2	Evan P. Kyba Department of Chemistry University of Texas Austin, Texas 78712
Synthesis of Novel Fluorine Compounds - New Experimental Challenges in Elemental Fluorine Chemistry (AJM) AFOSR-78-3658, 2303/B2	Richard J. Lagow Department of Chemistry University of Texas Austin, Texas 78712

Structure of Solid Surfaces in Wear Situations (AJM) AFOSR-81-0005, 2303/A2	James L. Lauer Department of Mechanical Engineering Rensselaer Polytechnic Institute Troy, New York 12181
Infrared Chemiluminescence Studies of Ion-Molecule Reactions in a Flowing Afterglow (WGT) AFOSR-78-3565, 2303/B1	Stephen R. Leone G. Barney Ellison Veronica M. Bierbaum Department of Chemistry University of Colorado Boulder, Colorado 80309
Analysis and Prediction of Experimental Results for Elementary Molecular Processes (WGT) AFOSR-81-0030, 2303/B1	Raphael D. Levine James L. Kinsey Department of Chemistry Massachusetts Institute of Technology Cambridge, Massachusetts 02139
Preparation & Properties of Halide Glasses and Glass-Polymer Composites (DRU) AFOSR-80-0059, 2303/A3	John D. Mackenzie Materials Department University of California Los Angeles, California 90024
Theoretical Studies of Relatively Rigid Polymer Chains (DRU) AFOSR-78-3683, 2303/A3	James E. Mark Department of Chemistry University of Cincinnati Cincinnati, Ohio 45221
Fabricable Polymers for Matrices and Adhesives which Are Extremely Stable to Heat, Oxidation and Hydrolysis (AJM) AFOSR-77-3112, 2303/B2	Carl S. Marvel Department of Chemistry University of Arizona Tucson, Arizona 85721
Study of the Chlorine-Basic Hydrogen Peroxide Reaction (AJM) AFOSR-81-0155, 2303/D9	Richard J. McCluskey Department of Chemical Engineering Clarkson College of Technology Potsdam, New York 13676
Energetic and Collision Dynamics of Electronic Transition Laser Systems (WGT) F49620-81-C-0097, 2303/B1	H. Michels Robert H. Hobbs United Technologies Research Center East Hartford, CT 06108

Mechanisms and Kinetics of Diphthalocyanine Electrode Processes (AJM) F49620-80-C-0060, 2303/B2	M. M. Nicholson Electronics Research Division Rockwell International Corp Anaheim, California 92803
Electronically Excited Molecular Oxygen (WGT) AFOSR-79-0088, 2303/B1	Elmer A. Ogryzlo Department of Chemistry University of British Columbia 2036 Main Mall Vancouver, B.C. Canada V6T-1Y6
Electrochemistry and Electrochemical Methodology in Molten Salts (DWE) AFOSR-81-0007, 2303/A1	Robert A. Osteryoung Janet G. Osteryoung Department of Chemistry State University of New York Buffalo, New York 14214
Synthesis of Phosphatriazines for Potential High Temperature Fluids and Elastomers Applications (AJM) F49620-79-C-0037, 2303/B2	Kay L. Paciorek Chemical & Materials Research Ultrasystems, Inc. Irvine, California 92664
The Molecular Dynamics of Reactions Forming Electronically Excited Products (WGT) AFOSR-81-0027, 2303/B1	John C. Polanyi Department of Chemistry University of Toronto Toronto, Ontario, Canada M5S 1A1
Excited State Chemistry of Halogen Azides (WGT) F49620-79-C-0053, 2303/B1	A. T. Pritt, Jr. Rockwell International Science Center Thousand Oaks, CA 91360
Studies in Non-Equilibrium Statistical Mechanics (WGT) AFOSR-78-3724, 2303/B1	Herschel Rabitz Stuart D. Augustin Department of Chemistry Princeton University Princeton, New Jersey 08540
Computational Study of Nonadiabatic Effects in Atom-Molecule Reactive Scattering (WGT) F49620-81-C-0046, 2303/B1	Michael J. Redmon Research Department Chemical Dynamics Corporation Columbus, Ohio 43220
Experimental and Theoretical Studies of Molecular Dynamics (WGT) AFOSR-81-0029, 2303/B1	Stuart A. Rice Department of Chemistry University of Chicago Chicago, Illinois 60637

Theory and Experiments on Chemical Dynamics and Instabilities (WGT) AFOSR-81-0125, 2303/B1	John Ross Department of Chemistry Stanford University Stanford, California 94305
Basic Research in Novel Inorganic Reagents and Fluorocarbon Chemistry (AJM) F49620-81-C-0020, 2303/B2	C. J. Schack Rocketdyne Division Rockwell International Canoga Park, CA 91304
Nonlinear Interactions Between the Pumping Kinetics, Fluid Dynamics and Optical Resonator of CW Fluid Flow Lasers (WGT) AFOSR-80-0133, 2303/B1	Lee H. Sentman M. Nayfeh Aeronautical and Astronautical Engineering University of Illinois Urbana, Illinois 61801
Organosilicon Compounds and Organosilicon Polymer Intermediates (AJM) AFOSR-79-0007, 2303/B2	Dietmar Seyferth Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139
Impact Initiated Damage in Laminated Composites (DRU) F49620-80-C-0050, 2303/A3	A. V. Sharma Department of Mechanical Engineering North Carolina A&T University Greensboro, N. C. 27422
Innovative Detection Separation and Sampling Techniques for Trace Analysis by Gas Chromatography (DWE) AFOSR-80-0011, 2303/A1	Robert E. Sievers Department of Chemistry University of Colorado Boulder, Colorado 80309
Reactive Atomic Species Generated at High Temperatures and Their Low Temperatures Reactions to Form Novel Substances (AJM) AFOSR-79-0063, 2303/B2	Philip S. Skell Department of Chemistry Pennsylvania State University University Park, PA 16802
Spectroscopy and Chemistry of Molecules with High Vibrational Energy Content (WGT) AFOSR-78-3725, 2303/B1	Jeffrey I. Steinfeld Department of Chemistry Massachusetts Institute of Technology Cambridge, MA 02139

High Dose Ion Implantation on Titanium, Aluminum, and Titanium-Aluminum Alloys with Application to Oxide and Nitride Formation (LEM) AFOSR-79-0011, 2303/A2	James R. Stevenson M. W. Ribarsky Keith Legg School of Physics Georgia Institute of Technology Atlanta, Georgia 30332
The Role of Coupling Agents in Metal-Polymer Adhesion (LEM) F49620-79-C-0085, 2303/A2	C. S. P. Sung N. H. Sung Department of Materials Science & Engineering Massachusetts Institute of Technology Cambridge, MA 02139
Structural and Dynamic Studies of Materials Possessing High Energy Content (AJM) AFOSR-81-0013, 2303/B2	Nicholas J. Turro Department of Chemistry Columbia University New York, New York 10027
Microstructure of Amorphous and Semi-Crystalline Polymers (DRU) AFOSR-81-0011, 2303/A3	Donald R. Uhlmann Department of Materials Science & Engineering Massachusetts Institute of Technology Cambridge, MA 02139
Radiation and Laser Potential of Home- and Hetero-Nuclear Rare Gas Diatomic Molecules (WGT) AFOSR-77-3137, 2303/B1	W. C. Walker Y. Tanaka Department of Physics University of California Santa Barbara, CA 93106
Correlation of Electrode Kinetics with Surface Structure (DWE) AFOSR-80-0271, 2303/A1	Michael J. Weaver Department of Chemistry Michigan State University East Lansing, Michigan 48824
Organosilicon Chemistry (AJM) AFOSR-80-0006, 2303/B2	William P. Weber Department of Chemistry University of Southern California Los Angeles, CA 90007

Chemical Reactions and Properties of Organosilicon Compounds Related to New Materials (AJM) AFOSR-78-3570, 2303/B2	Robert C. West Department of Chemistry University of Wisconsin Madison, Wisconsin 53706
Atomic and Molecular Gas Phase Spectrometry (DWE) F49620-80-C-0005, 2303/A1	James D. Winefordner Department of Chemistry University of Florida Gainesville, Florida 32611
X-Ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) (DWE) AFOSR-80-0002, 2303/A1	Nicholas Winograd Department of Chemistry Pennsylvania State University University Park, PA 16802
Kinetic Studies of Gas Phase Free Radicals (WGT) AFOSR-78-3693, 2303/B1	Curt Wittig Department of Electrical Engineering University of Southern California Los Angeles, CA 90007
Polybenzothiazoles - Synthesis and Characterization (DRU) F49620-81-K-0003, 2303/A3	James E. Wolfe Chemistry Laboratory SRI International Menlo Park, California 94025
A First Principles Approach to Electronic Energy Transfer Processes in Reactions of the Form Me + O-A = MeO + A (WGT) AFOSR-79-0073, 2303/B1	David R. Yarkony Department of Chemistry The Johns Hopkins University Baltimore, Maryland 21218
State Identification of Reaction Products (WGT) AFOSR-81-0053, 2303/B1	Richard N. Zare Department of Chemistry Stanford University Stanford, California 94305

RESEARCH EFFORTS COMPLETED IN FY81

CHEMISTRY

Alphabetical by Principal Investigator

Photoionization of Molecular Clusters (WGT) AFOSR-78-3638, 2303/B1	R. P. Andres J. M. Calo Department of Chemical Engineering Princeton University Princeton, NJ 08544
Diagnostics and Chemical Applications of Multiphoton Absorption Processes (WGT) AFOSR-77-3279, 2303/B1	Sidney W. Benson Department of Chemistry University of Southern California Los Angeles, CA 90007
Light Scattering from Macromolecular Systems - Molecular Crystals and Polymers (DRU) AFOSR-77-3317, 2303/A3	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, CO 80523
Property-Structure-Processing Relations in Polymeric Materials (DRU) AFOSR-77-3404, 2303/A3	Guy C. Berry Hershel Markovitz Chemistry Department Carnegie-Mellon University Pittsburgh, PA 15213
Model Studies of Energetic Compounds (AJM) AFOSR-80-0104, 2303/D9	W. Robert Carper Department of Chemistry Wichita State University Wichita, KS 67208
Effects of Surface Morphology and Chemical Composition on the Durability of Adhesively Bonded Aluminum Structures (LEM) F49620-78-C-0097, 2303/A2	G. D. Davis (T. S. Sun) Martin Marietta Corporation Martin Marietta Laboratories 1450 South Rolling Road Baltimore, MD 21227
Picosecond Laser Studies of Excited State Proton Transfer (AJM) AFOSR-77-3407, 2303/B2	Kenneth B. Eisenthal Department of Chemistry Columbia University New York, New York 10027

Time Resolved Spectroscopy of Reactive Chemical Systems (DWE) AFOSR-78-3617, 2303/A1	W. G. Fateley R. M. Hammaker Department of Chemistry Kansas State University Manhattan, KS 66506
The Structure and Properties of Polymeric Materials (DRU) AFOSR-77-3293, 2303/A3	P. J. Flory Department of Chemistry Stanford University Stanford, CA 99305
Chemical and Physical Aspects of Mesophase Formation during Carbon-Carbon Processing (DRU) F49620-78-C-0006	J. J. Gebhardt Re-entry Systems Division General Electric Company Philadelphia, PA 19101
Solute-Gas Equilibria in Multi-Organic Aqueous Systems (AJM) AFOSR-81-0074, 2303/D9	James Gossett Environmental Engineering Department Cornell University Ithaca, NY 14853
Ion-Molecule Reactions Involving Atmospheric Cluster Ions (WGT) AFOSR-80-0116, 2303/D9	Michael Henchman Department of Chemistry Brandeis University Waltham, MA 02254
Electrochemical Impregnation for the Fabrication of Cadmium Electrodes (DWE) AFOSR-79-0104, 2303/A1	Y. K. Kao Department of Electrical Engineering University of Cincinnati Cincinnati, OH 45221
Analysis of Lubricant Films in Bearings under Incipient Failure Conditions (LEM) AFOSR-78-3473, 2303/A2	James L. Lauer Department of Mechanical Engineering Aeronautical Engineering & Mechanics Rensselaer Polytechnic Institute Troy, NY 12181
Laser Hole Burning Spectroscopy: A High Resolution Probe of Molecular Environments (DRU) F49620-79-C-0108, 2303/A3	R. M. Macfarlane IBM Research Laboratory San Jose, CA 95193

Chemical Structure by Laser-Produced X-Rays (DWE) AFOSR-78-3575, 2303/A1	P. J. Mallozzi R. E. Schwerzel Battelle Memorial Institute 505 King Avenue Columbia, OH 43201
A Search for New Fuel Components in Explosive Mistures with Ammonium Nitrate (AJM) AFOSR-80-0134, 2303/D9	Maurice C. Neveu Department of Chemistry State University of New York Fredonia, NY 14063
Solid State Reactions in Polymeric Materials (DRU) AFOSR-78-3676; F49620-79-C-0229; AFOSR-80-0287, 2303/A3	Paras N. Prasad Department of Chemistry State University of New York Buffalo, NY 14214
Study of Non-Radiating Species in Metal + Oxidant Chemiluminescent Flames (WGT) F49620-79-C-0023, 2303/B1	James Gary Pruett Department of Chemistry University of Pennsylvania Philadelphia, PA 19174
Theory and Experiments on Chemical Dynamics and Chemical Instabilities (WGT) AFOSR-81-0125, 2303/B1	John Ross Department of Chemistry Stanford University Stanford, CA 94305
New Solid Superionic Conductors Containing Cu$^+$, GA$^+$, In$^+$ and Tl$^+$ (DWE) AFOSR-77-3227, 2303/A1	Duward F. Shriver Department of Chemistry Donald H. Whitmore Department of Materials Science & Engineering Northwestern University Evanston, IL 60201
Basic Studies Relative to the Syntheses of Unsymmetrical Dimethylhydrazine and Monomethylhydrazine by Chloramination (AJM) AFOSR-76-2915; AFOSR-80-0007, 2303/B2	Harry H. Sisler Department of Chemistry University of Florida Gainesville, FL 32611
Lithium Based Anodes for Solid State Batteries (AJM) AFOSR-77-3460, 2303/B2	B. C. H. Steele Department of Metallurgy & Materials Science Imperial College London, SW7 2BP UK

Synthesis of New Inorganic and Organometallic Materials (AJM) AFOSR-76-3102, 2303/B2	F. Gordon A. Stone Department of Inorganic Chemistry The University of Bristol Bristol BS8 1TS UK
Analytical Approach to the Selection of the Reaction Coordinate in the Calculation of Reaction Profiles (AJM) AFOSR-81-0114, 2303/D9	Almon G. Turner Department of Chemistry University of Detroit 4001 W. McNichols Road Detroit, MI 48221
Structural and Dynamic Studies of Materials Possessing High Energy Content (AJM) AFOSR-78-3502, 2303/B2	Nicholas J. Turro Department of Chemistry Columbia University New York, NY 10027
Microstructure of Amorphous and Semi-Crystalline Polymers (DRU) AFOSR-77-3226, 2303/A3	D. R. Uhlmann Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, MA 02139
Stabilization of Acrylic Fibers and Microstructure of Carbon-Carbon Composites (DRU) AFOSR-77-3466, 2303/A3	D. R. Uhlmann Department of Materials Science and Engineering Massachusetts Institute of Technology Cambridge, MA 02139
Applied Quantum Chemistry of Nonmetallic Materials (AJM) AFOSR-77-3145, 2303/B2	John Van Wazer Department of Chemistry Vanderbilt University Nashville, TN 37235
Experimental Studies of the State-to-State Chemical Dynamics of Reactions Involving Air Triatomics (WGT) AFOSR-77-3348, 2303/B1	Milo E. Whitson, Jr. The Aerospace Corporation P.O. Box 92957 Los Angeles, CA 90009
Alkaline Earth-Noble Gas Excimers (WGT) F49620-79-C-0049, 2303/B1	John J. Wright Department of Physics University of New Hampshire Durham, NH 03824

The State Identification of Reaction Products (WGT) AFOSR-77-3363, 2303/B1	Richard N. Zare Department of Chemistry Stanford University Stanford, CA 94305

ACTIVE RESEARCH EFFORTS

ATMOSPHERIC SCIENCES

As of 1 Oct 1981

Alphabetical by Principal Investigator

Analysis and Prediction of Severe Storm Environment (TSC) AFOSR-79-0125, 2310/A1	R. A. Anthes T. N. Carlson Department of Meteorology Pennsylvania State University University Park, PA 16802
MITHRAS Magnetosphere-Ionosphere-Thermosphere Radar Studies Using Three High-Latitude Incoherent-Scatter Stations (TSC) F49620-81-C-0042, 2310/A2	Odile de la Beaujardiere Radio Physics Laboratory SRI International 333 Ravenswood Avenue Menlo Park, CA 94025
Behavior of the Atmosphere in the Desert Planetary Boundary Layer (TSC) AFOSR 81-0126, 2310/A1	Louis Berkofsky Meteorology Department Ben Gurion University of the Negev Beer-Sheva, Israel
Dynamic-Chemical Coupling in the Mesosphere and Lower Thermosphere (TSC) AFOSR-81-0090, 2310/A2	Jeffrey M. Forbes Space Data Analysis Laboratory Boston College Newton, Massachusetts 02159
Shear Excitation of Atmospheric Gravity Waves (TSC) F49620-81-C-0009, 2310/A1	David Fritts Science Department Physical Dynamics, Inc. Bellevue, WA 98009
Studies of Extratropical Cyclonic Storms; The CYCLES Project (TSC) AFOSR-ISSA-82-00018, 2310/A1	Peter V. Hobbs Department of Atmospheric Sciences University of Washington Seattle, WA 98195
Construction of University of Missouri-Rolla's Full Scale Cloud Simulation Chamber (TSC) F49620-80-C-0090, 2310/A1	James J. Kassner, Jr. D. R. White Department of Physics University of Missouri-Rolla Rolla, Missouri 65401

Analysis of the NOAA Alaskan MST Radar System Data (TSC) AFOSR-80-0020, 2310/A2	Michael C. Kelley D. T. Farley M. Larsen Department of Electrical Engineering Cornell University Ithaca, New York 14853
Light Scattering and Absorption Properties of Ice Clouds for Visible and Infrared Laser Wavelengths (TSC) F49620-79-C-0198, 2310/A1	Kuo-Nan Liou Kenneth Sassen Department of Meteorology University of Utah Salt Lake City, Utah 84112
Shear-Induced Turbulence by MST Radar (TSC) AFOSR-80-0286, 2310/A1	Gerald J. Romick Kolf Jayaweera Geophysical Institute University of Alaska Fairbanks, Alaska 99701
High Time Resolution Thermospheric Temperature and Wind Studies in the Arctic (TSC) AFOSR-80-0240, 2310/A2	Gerald J. Romick Geophysical Institute University of Alaska Fairbanks, Alaska 99701
Meteorology (TSC) AFOSR-ISSA-81-00040, 2310/A1	Stanley Ruttenberg Director, Office of Scientific Program Development University Corporation for Atmospheric Research Boulder, CO 80307
Upper Atmospheric Structure and Dynamics (TSC) AFOSR-ISSA-81-0039, 2310/A2	Gene E. Tallmadge Radio Physics Laboratory SRI International 333 Ravenswood Avenue Menlo Park, CA 94025
Latitudinal Variations of Auroral Zone Ionization Distributions (TSC) F49620-80-C-0014, 2310/A2	James Vickrey Radio Physics Laboratory SRI International Menlo Park, CA 94025
Phase Fluctuations of Transionospheric Signals under Multiple Scattering Conditions (TSC) AFOSR-80-0187, 2310/A2	Bruce J. West V. Seshadri La Jolla Institute P.O. Box 1434 La Jolla, CA 92038

Low Frequency Light Scattering in Extended Chain Polymers (DRU) AFOSR-77-3317, 2303/A3	Elliot R. Bernstein Department of Chemistry Colorado State University Fort Collins, Colorado 80521
Solid State Reactions in Polymeric Materials (DRU) AFOSR-80-0287, 2303/A3	Paras N. Prasad Department of Chemistry State University of New York Buffalo, New York 14260
Chemical Structure by Laser-Produced X-Rays (DWE) AFOSR-78-3575, 2303/A1	Robert E. Schwerzel Battelle Memorial Institute 505 King Avenue Columbus, Ohio 43201
X-Ray Photoelectron Spectroscopy (XPS) and Secondary Ion Mass Spectrometry (SIMS) (DWE) AFOSR-80-0002, 2303/A1	Nicholas Winograd Department of Chemistry Pennsylvania State University University Park, PA 16802

RESEARCH EFFORTS COMPLETED IN FY81

ATMOSPHERIC SCIENCES

Alphabetical by Principal Investigator

The Morphology of Stratospheric Planetary Waves (TSC) F49620-78-C-0036; F49620-79-C-0160, 2310/A2	Arthur D. Belmont Meteorology Department Research Division Control Data Corporation Minneapolis, MN 55440
Low Level Convergence and the Prediction of Precipitation (TSC) AFOSR-ISSA-79-0028; AFOSR-ISSA-80-0029 (NSF Grant ATM-78-08865), 2310/A1	Stanley A. Changnon, Jr. Bernice Ackermann Illinois State Water Survey University of Illinois P.O. Box 232 Urbana, IL 61801
Structure of the Upper Atmosphere (TSC) AFOSR-77-3223, 2310/A2	Jeffrey M. Forbes Department of Physics Boston College Chestnut Hill, MA 02167
Geophysical Analysis of Coherent Satellite Scintillation Data (TSC) F49620-78-C-0014, 2310/A2	Edward J. Fremouw Physical Dynamics, Inc. P.O. Box 3027 Bellevue, WA 98009
Analysis of Severe Weather Using Digital Doppler and Non-coherent Radar Data (TSC) AFOSR-80-0063, 2310/A1	George Huebner Department of Meteorology Texas A&M University College Station, TX 77843
Experiments in Regional Scale Numerical Weather Prediction Including Use of SESAME '79 Data (TSC) F49620-79-C-0208, 2310/A1	Carl W. Kreitzberg Department of Physics and Atmospheric Sciences Drexel University Philadelphia, PA 19104
Propagation of Transient Signals through Nonlinear Ionized Media (TSC) AFOSR-78-3729, 2310/A2	Robert E. McIntosh Electrical and Computer Engineering University of Massachusetts Amherst, MA 01002

Aerosol Profiles vs Meteorological Conditions (TSC) AFOSR-77-3228, 2310/A1	Reinhold Reiter Fraunhofer Institute for Environmental Research Kreuzeckbahnstrasse 19 Garmisch-Partenkirchen Federal Republic of Germany
Scattering by Nonspherical Particles (TSC) AFOSR-MIPR-78-0016; 79-0011; 80-0015 (To ARO Contract DAAG 29-78-G-0024), 2310/A1	Donald W. Schuerman Space Astronomy Laboratory University of Florida 1816 NW G Street Gainesville, FL 32601
Atmospheric Absorption of Radiation by Water (TSC) AFOSR-80-0058, 2310/D9	Richard H. Tipping Physics Department University of Nebraska Omaha, NE 68182

Air Force Laboratory Chemical Sciences

Research Projects

1. TITLE: Physical Chemistry and Electrochemistry

2. PRINCIPAL INVESTIGATOR: Capt John L. Williams
Frank J. Seiler Research Laboratory
Air Force Academy, CO 80840

3. ABSTRACT OF OBJECTIVES:

Provide scientific basis for the development of high current density and high energy density electrochemical power supplies.

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1. TITLE: Energetic Materials Chemistry Research

2. PRINCIPAL INVESTIGATOR: Dr. John S. Wilkes
Frank J. Seiler Research Laboratory
Air Force Academy, CO 80840

3. ABSTRACT OF OBJECTIVES:

Discover new energetic materials for solid propellant formulations to enhance missile payload and range extension capabilities. Understand the thermochemical and photochemical decomposition mechanisms of explosives. Discover new low-hydrogen content explosives.

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1. TITLE: Molecular Dynamics

2. PRINCIPAL INVESTIGATOR: Major Myron DeLong
Frank J. Seiler Research Laboratory
Air Force Academy, CO 80840

3. ABSTRACT OF OBJECTIVES:

Understand the thermochemical and photochemical decomposition mechanisms of explosives and propellants. Understand the chemical production of singlet delta oxygen used in pumping the oxygen-iodine laser system. Identify specific molecules in chemiluminescent flames which may be potential laser candidates.

1. TITLE: Upper Atmosphere Chemistry

2. PRINCIPAL INVESTIGATOR: Dr. John F. Paulson
Air Force Geophysics Laboratory
Hanscom AFB, MA 01731

3. ABSTRACT OF OBJECTIVES:

Measure cross sections and rate coefficients for reactions between atmospheric ion species and neutral molecules. The ions studied will include simple and clustered (solvated) species, both positive and negative. Study mutual neutralization reactions between positive and negative ions. Study photoabsorption and photodissociation reactions of neutrals and ions, measure the cross sections, and identify the products. Calculate the product energy levels and reaction hypersurfaces for simple ion-neutral reactions of atmospheric importance.

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1. TITLE: Plume Atmosphere Interactions

2. PRINCIPAL INVESTIGATOR: Mr. Alfred Rahbee
Air Force Geophysics Laboratory
Hanscom AFB, MA 01731

3. ABSTRACT OF OBJECTIVES:

Investigate and measure vibrational excitation cross sections for high-velocity collisions of major rocket plume species with atmospheric species. The results are ultimately used in plume analysis and prediction.

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1. TITLE: Synthesis of Propellant Ingredients

2. PRINCIPAL INVESTIGATOR: Capt Scott Shackelford
Air Force Rocket Propulsion Laboratory
Edwards AFB, CA 93523

3. ABSTRACT OF OBJECTIVES:

Conduct original synthesis of new, energetic propellant ingredient materials. Synthesize new propellant curatives, measure migration rates of mobile ingredients and improve techniques to determine polymer properties.

1. TITLE: Surface Phenomena

2. PRINCIPAL INVESTIGATOR: Dr. Trice W. Haas
Air Force Wright Aeronautical Laboratories
Materials Laboratory
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Elucidate the basic chemical and physical factors affecting the control, activation, lifetime, and poisoning of various types of low work function cathodes (oxide, dispenser, matrix) for use in travelling wave tubes. Determine the surface chemical factors which control the growth, perfection, and electrical characteristics of thin film silicon grown epitaxially on sapphire substrates. Investigate surface chemical interactions between various metals used as interconnection and contact materials in solid state devices and silicon and silicon dioxide surfaces.

- -

1. TITLE: Fluids and Lubricants Synthesis

2. PRINCIPAL INVESTIGATOR: Dr. Christ Tamborski
Air Force Wright Aeronautical Laboratories
Materials Laboratory
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Synthesize new fluid materials based on silahydrocarbons and synthetic hydrocarbons and determine the structure-property correlations to provide the fluid technology base for new and advanced fluids and lubricant materials. Synthesize new additive materials for the new fluids synthesized above in order to improve specific physical and chemical properties; e.g., viscosity index improvers, anti-oxidants and anti-corrosion additives.

1. TITLE: Basic Factors in the Synthesis of Macromolecular Materials

2. PRINCIPAL INVESTIGATOR: Dr. Richard L. Van Deusen
Air Force Wright Aeronautical Laboratories
Materials Laboratory
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Provide the basic scientific knowledge of polymers, polymeric compositions, and composites that will result in plastic and elastomeric base materials for the development of new structural and ablative composites, sealants, seals, transparent innerlayers, adhesives, and coatings for advanced aircraft and missiles.

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1. TITLE: Elastochemistry

2. PRINCIPAL INVESTIGATOR: Dr. D. Fritts
Air Force Wright Aeronautical Laboratories
Aero-Propulsion Laboratory
Wright-Patterson AFB, OH 45433

3. ABSTRACT OF OBJECTIVES:

Extend satellite and aircraft battery life while reducing cost and maintenance requirements. Studies will include nickel-cadmium, nickel-zinc and nickel-hydrogen couples with emphasis on improving performance and cyclic life. Develop a high energy density rechargeable battery using nonaqueous electrolyte and provide the technology for long shelf life primary batteries for electronic jammers, life support equipment and munitions. Investigate electrode/electrolyte combinations which can provide the potential for very high rate discharges (50-100 times rated current) for short periods of time coupled with high energy density during normal operation. Conduct basic studies in support of the development of high volumetric energy density batteries for future electronic applications. Evaluate low-melting temperature solvent systems containing inorganic and organic chlorides and bromides to establish their liquidus temperatures, conductivity and electrochemical potential.

1. TITLE: Chemical Laser Processes

2. PRINCIPAL INVESTIGATOR: Dr. Leroy E. Wilson
Air Force Weapons Laboratory
Kirtland AFB, NM 87117

3. ABSTRACT OF OBJECTIVES:

Theoretically and experimentally determine the physical chemistry parameters of rotational energy transfer rate, quenching rate, V-V exchange, and line broadening parameters of an optically pumped DF resonance transfer cell. Experimentally determine the HF/DF high vibration state relaxation rate constants using double resonance technique and develop new experimental and theoretical techniques for determining state to state reaction rates. Analysis and experiments will be conducted to determine limiting processes when radiative times become comparable to kinetic times. Experimentally and theoretically determine multipulse HF/DF laser kinetics to understand the effect of rotational, kinetic rates on pulse laser characteristics. Measure the effect of anomalous dispersion on the output beam of a high energy chemical laser during power broadening.

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1. TITLE: Electronic Transition Chemical Laser Concepts

2. PRINCIPAL INVESTIGATOR: Dr. Steve Davis
Air Force Weapons Laboratory
Kirtland AFB, NM 87117

3. ABSTRACT OF OBJECTIVES:

Identify and explore new candidates for development of efficient, high-energy, electronic transition, gas phase chemical lasers. The spectroscopy of the halogens and the spectroscopy and reaction kinetics of the interhalogens are being emphasized.

Air Force Geophysics Laboratory
Hanscom AFB, MA 01731

Atmospheric Sciences

Research Projects

1. TITLE: Molecular and Aerosol Properties of the Atmosphere

2. PRINCIPAL INVESTIGATOR: Dr. George A Vanasse

3. ABSTRACT OF OBJECTIVES:

Obtain laboratory high-resolution, high-temperature data of atmospheric constituents, and perform balloon-borne measurements of stratospheric emission using a high-resolution cryogenic interferometer. Conduct research leading to improved molecular parameters for use in the theoretical spectroscopy, for updating the transmission/emission codes, and for computing molecular absorption/emission line widths and shapes. Develop models of the optical properties of aerosols in order to calculate such parameters as beam attenuation, angular scattering intensities, polarization, path radiance and contrast transmission. Perform experimental and theoretical studies in order to correlate aerosol particle refractive index, size distribution, and concentration with meteorological and environmental conditions.

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1. TITLE: Upper Atmosphere Composition

2. PRINCIPAL INVESTIGATOR: Dr. Rocco S. Narcisi

3. ABSTRACT OF OBJECTIVES:

Measure the ionospheric species and concentrations in the D- and E-regions during solar-disturbed periods (geomagnetic storms, solar proton events (SPE), etc.) to determine upper atmospheric physical-chemical processes important to LF/VLF/HF communications. Measure ionospheric composition and dynamics in a coordinated program to define the ionosphere during continuous aurora to determine if electron density profiles can be accurately predicted from remotely sensed optical measurements. Develop models of ion/electron structure utilizing physical-chemical and transport processes in order to describe the twilight and daytime disturbed high-latitude ionosphere. Perform equatorial rocket programs to artifically induce spread-F conditions which degrade satellite transmissions. Create irregularities through rocket explosive water releases and measure the resulting disturbance in-situ with instrumented rockets, ground-based and aircraft radars, ionosondes, optical sensors, and satellite transmission scintillations.

1. TITLE: Infrared Atmospheric Processes

2. PRINCIPAL INVESTIGATOR: Dr. Randall E. Murphy

3. ABSTRACT OF OBJECTIVES:

Study and define the processes that control infrared emissions in auroral and nuclear-disturbed atmospheres. Determine the spectral, spatial and temporal character of airglow infrared emissions with and without solar illumination.

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1. TITLE: Cloud Physics

2. PRINCIPAL INVESTIGATOR: Dr. Arnold A. Barnes

3. ABSTRACT OF OBJECTIVES:

Measure, describe and model the microphysical characteristics of cloud and precipitation systems.

- -

1. TITLE: Remote Ionospheric Mapping

2. PRINCIPAL INVESTIGATOR: Dr. J. R. Jasperse

3. ABSTRACT OF OBJECTIVES:

Develop methods for determining the electron density profile from an analysis of the reflected and/or transmitted components of an electromagnetic wave incident from outside the Earth's ionosphere. Develop quantitative methods for determining the electron density profile using a combination of theoretical analysis and data obtained from satellite observations. Develop methods for determining the amplitude and phase of an electromagnetic wave propagating through the Earth's ionosphere whose dielectric properties are given.

1. TITLE: Atmospheric Dynamic Models

2. PRINCIPAL INVESTIGATOR: Dr. Chien-hsiung Yang

3. ABSTRACT OF OBJECTIVES:

Formulate a dynamic-numerical model of the moist atmosphere on a global scale to serve as a research vehicle to understand the dynamics and physics of the atmosphere. Understand and model medium (meso) scale dynamics and the interactions between this scale and both the larger and the smaller scale processes.

A TRIBUTE TO DR MICHAEL CLYNE

During this year we lost one of our very distinguished colleagues when Michael Clyne of Queen Mary College, London, passed away. Michael's distinguished scientific career began at Trinity College, Cambridge, in 1956. He graduated with first class honor in 1959. From 1959-1962 he completed his PhD in chemistry under the supervision of B. A. Thrush. He received his MA from Cambridge in 1963. He was a Lecturer in Physical Chemistry at the University of East Anglia from 1964-1966. He became a Lecturer in Physical Chemistry at Queen Mary College in 1966 and was promoted to a Reader in Physical Chemistry in 1977.

Michael Clyne's association with AFOSR began with his Window on Science visit to the Air Force Weapons Laboratory in 1974. At that time Air Force researchers at the Weapons Laboratory were studying several chemiluminescent reactions including those producing excited electronic states in several interhalogen molecules. Michael Clyne had performed experiments in this area previous to his visit and was already a recognized expert in halogen kinetics.

Shortly after his visit Michael submitted a proposal to AFOSR. From this proposal grew a very productive interaction. Early in 1975 Michael began to incorporate a tunable dye laser into his apparatus in order to study kinetics of the excited states of the interhalogen molecule BrF. He also began a detailed study of the production of excited states in NF. Both interhalogens and NF have received intensive attention at several laboratories for their potential as electronic transition chemical lasers.

It was in the area of what Michael liked to call "quantum resolved dynamics of excited states" that his group was most productive. His innovative incorporation of narrow band dye lasers to study radiative lifetimes and collisional phenomena of excited states led to a comprehensive and systematic investigation of several halogen and interhalogen molecules. Predissociation phenomena and dissociation energies combined with collisional quenching and energy transfer rates, all determined from these studies, have greatly extended our knowledge of excited state dynamics. His extensive results have also been of tremendous practical importance to Air Force programs. For example, Michael's results on IF have led to successful lasing demonstrations and this molecule is now being intensively studied as a visible chemical laser candidate.

Michael's detailed kinetics research on NF has led to an understanding of extremely efficient chemiluminescence reactions. The molecule NF has also received more than considerable attention as an electronic transition laser candidate system.

In addition to being a scientist of international stature, he was an exceptionally talented teacher. In his interactions with both his students and with his research group he was uncompromising in his insistence on thoroughness and excellence. His enthusiasm rubbed off onto his entire research group. Although insisting on these high standards, Michael was an extremely pleasant and likeable person. He was always receptive to new ideas. He was a great source of inspiration to all who knew him.

The extremely fruitful association of Michael Clyne with AFOSR was only a small fraction of his total scientific and academic contributions.

Dr. Steven J. Davis, Research Physicist, AFWL

CHEMICAL TECHNIQUES

Denton W. Elliott

The Chemical Techniques program's purpose is to assist in developing new and improved instrumentation and methods which will lead to new fundamental information on the properties and behavior matter. This is to be accomplished by the selection of those ideas of top scientists who are applying the new techniques to probe deeper, at faster rates, at extreme temperatures and with higher resolution and sensitivity into the sub-molecular and sub-atomic regions.

Because of the high relevance to Air Force needs, emphasis in this program is given to electrochemistry and detection. The requirements of the Air Force for electrochemical power devices with higher energy, lighter weight, longer life, and more reliability provide the basis for emphasis in the electrochemistry area.

The category of detection has Air Force implications across the board in the understanding of the scientific principles involved in the sensing and detection of the chemical and physical properties of the environment and of the materials of which it is comprised. An example of accomplishments in this program area is cited.

At the Battelle Columbus Laboratories, Drs. P. J. Mallozzi, R. E. Schwerzel, H. M. Epstein, et al., have come up with two powerful new structural analysis techniques, both involving the use of "soft" X-rays (energies of roughly 0.1 to 10 keV). The source of which they have termed "the poor man's synchrotron." Because these techniques can provide direct structural information on complex materials which lack long-range order, they promise to revolutionize the analysis of chemical structure.

One of these techniques is known as EXAFS (Extended X-ray Absorption Fine Structure). The essential features of EXAFS spectroscopy are depicted schematically in Figure 1. In EXAFS, the local configuration in the vicinity of a given atom embedded in a solid, liquid,or gas molecule is indicated by the tiny "wiggles" on the X-ray absorption edge of that atom. Because this fine structure is caused by the scattering of photoelectrons from the neighboring atoms, the mathematical analysis of the fine structure provides direct information about the positions of these atoms.

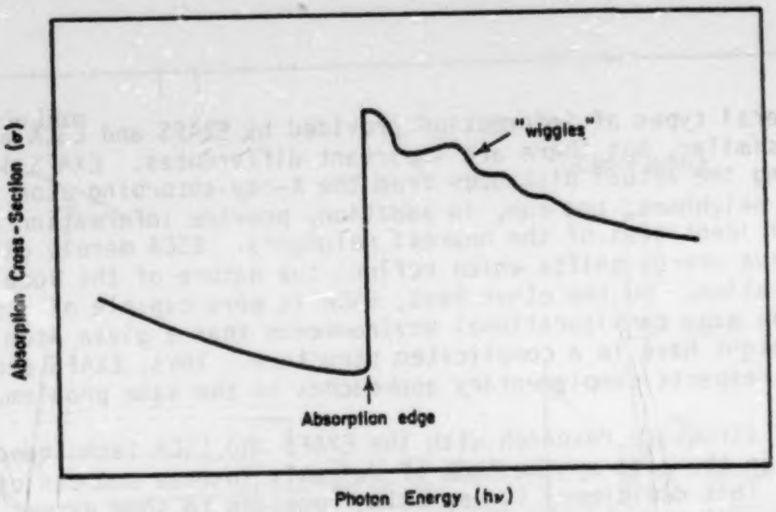

FIGURE 1. SCHEMATIC ILLUSTRATION OF AN EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) SPECTRUM

The other technique, which is depicted schematically in Figure 2, is a refinement of Electron Spectroscopy for Chemical Analysis (ESCA). In the ESCA approach, a highly monochromatic beam of X-rays strikes the surface of the sample, and the energy spectrum of the photoelectrons ejected from the surface is measured. The configuration in the vicinity of a given atom is indicated by the energy shifts in the photoelectron spectrum relative to the energy of an electron ejected from the same type of atom in free space.

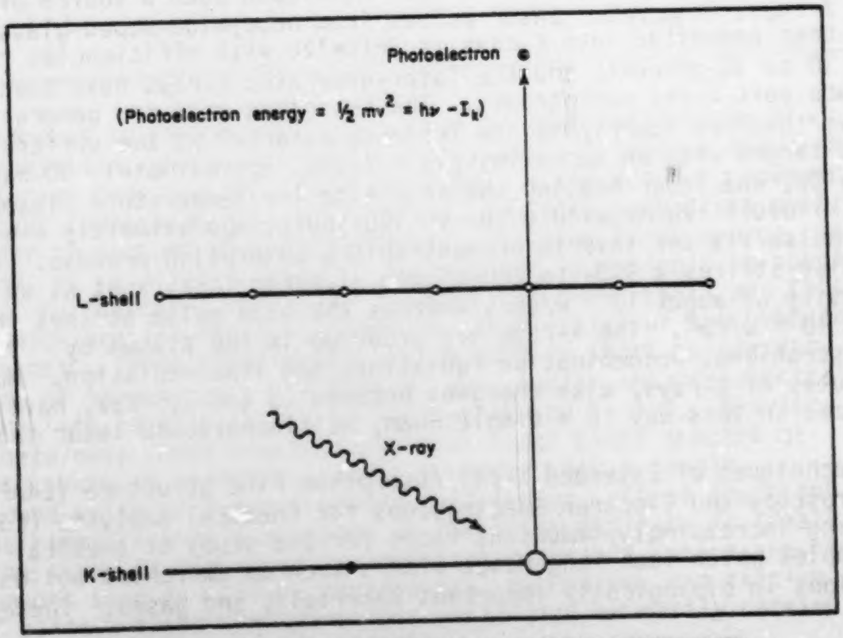

FIGURE 2. SCHEMATIC ILLUSTRATION OF ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA).

The general types of information provided by EXAFS and ESCA are thus rather similar, but there are important differences. EXAFS is capable of revealing the actual distances from the X-ray-absorbing atom to its nearest neighbors, and can, in addition, provide information about the chemical identities of the nearest neighbors. ESCA merely gives cumulative energy shifts which reflect the nature of the local configuration. On the other hand, ESCA is more capable of distinguishing among the many configurational environments that a given atom such as carbon might have in a complicated structure. Thus, EXAFS and ESCA are in many respects complementary approaches to the same problem.

Chemical structure research with the EXAFS and ESCA techniques has been limited in the past by the lack of suitably intense sources of soft X-rays. This deficiency is now being remedied to some extent by the increasing availability of synchrotron radiation, which has recently been harnessed in a number of X-ray test facilities throughout the world. However, synchrotron radiation is unlikely to be fully satisfactory as an X-ray source due to the enormous size and expense of the required facilities, and the corresponding need for most researchers to perform their experiments at remote locations.

The best hope for providing a relatively small, inexpensive, and transportable X-ray source for EXAFS and ESCA research lies in the development of laser-produced X-rays. High-powered laser pulses can provide high intensity X-rays with continuously tuneable wavelengths, as required for EXAFS, or with narrow spectral spikes, as required with ESCA.

Mallozzi and Schwerzel, et al., have developed such a source of available soft X-rays, Figure 3. Laser pulses from neodymium-doped-glass lasers have been converted into X-rays at Battelle with efficiencies ranging from 10 to 30 percent, and the laser-generated X-rays have been used to produce soft X-ray radiographs. The technique used for generating the X-rays involves vaporizing and ionizing material at the surface of a solid target with an approximately 1-joule, approximately 10-nanosecond prepulse, and laser heating the resulting low-temperature plasma to the multikilovolt regime with a 10- to 100-joule, approximately 1-nanosecond main pulse via the inverse bremsstrahlung absorption process. The prepulse strikes a 100- to 200-micron diameter focal spot at an incident intensity of about 10^{11} w/cm^2, whereas the main pulse strikes it at about 10^{14} w/cm^2. The X-rays are produced in the plasma by bremsstrahlung, recombination radiation, and line radiation. More than 20 joules of X-rays, with energies between .3 and 1.5 keV, have been produced in this way in a single beam, multinanosecond laser shot.

The techniques of Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy and Electron Spectroscopy for Chemical Analysis (ESCA) are becoming increasingly important tools for the study of chemical structure in samples which lack long-range order, such as amorphous solids, solutions in biologically important materials, and gases. These studies

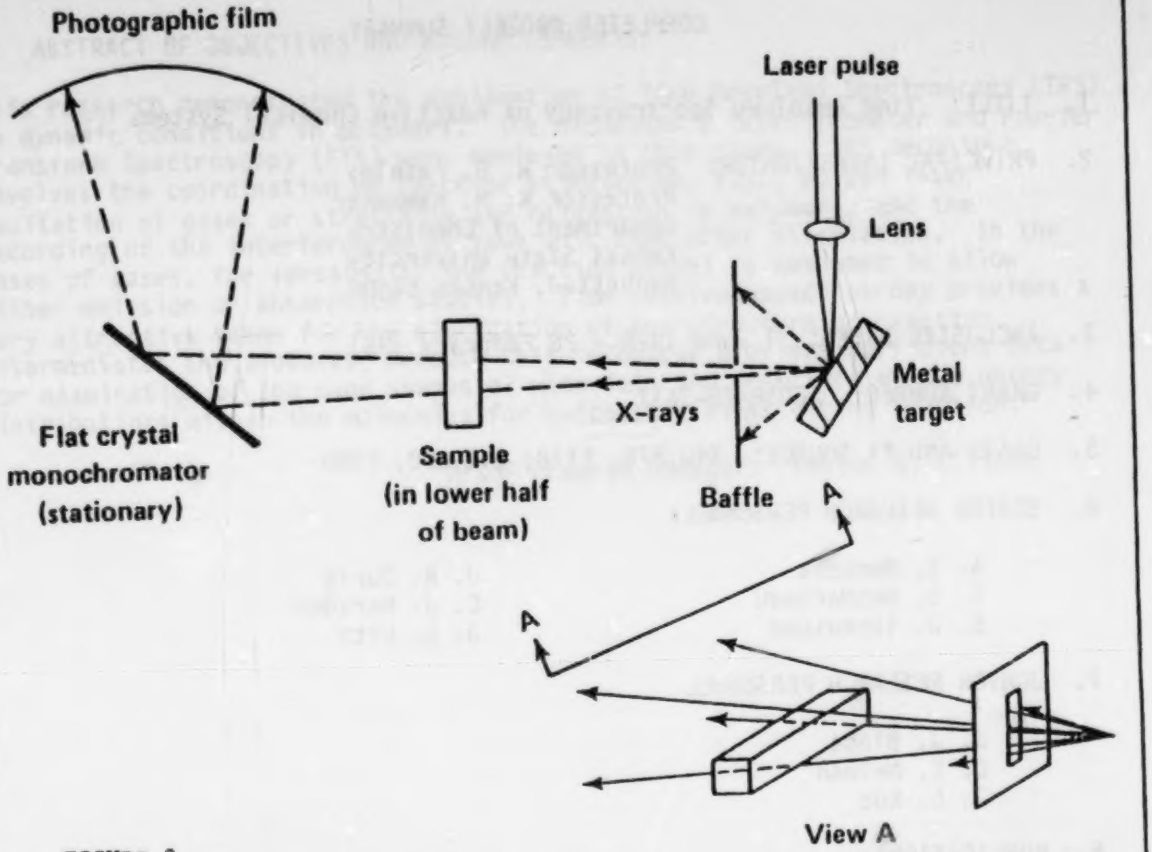
Photographic film
Laser pulse
Lens
Metal target
X-rays
Flat crystal monochromator (stationary)
Sample (in lower half of beam)
Baffle
A
A
View A

FIGURE 3

have gained impetus in recent years by virtue of the availability of synchrotron radiation, which provides a continuous and intense spectrum of the soft X-rays required for EXAFS and ESCA. A synchrotron, however, is an expensive, cumbersome source of X-rays, to which scientists must travel in order to perform their experiments. A laser X-ray source, on the other hand, is relatively compact, inexpensive, and simple to operate and maintain. Furthermore, there are a variety of novel EXAFS and ESCA experiments which are inherently beyond the capabilities of synchrotron radiation sources. These experiments, which require short pulsewidth, intense fluxes of low-energy (< 4 keV) X-rays, and/or intense spectral line structure, are ideally suited to laser-produced X-rays. Results obtained to date have shown conclusively that laser EXAFS spectra of light elements, such as aluminum, can be recorded with a single, multi-nanosecond pulse of laser-produced soft X-rays. It is important to note that the range of X-rays produced by the laser facility is ideally suited for the study of biologically-important materials, which are rich in light elements such as sulfur, phosphorous, magnesium, and calcium. The study of silicon-based semiconductors could also be easily carried out using X-rays of this energy distribution.

For additional information see Science, 19 Oct 1979, Vol 206, pp 353-355.

COMPLETED PROJECT SUMMARY

1. TITLE: Time Resolved Spectroscopy of Reactive Chemical Systems

2. PRINCIPAL INVESTIGATOR: Professor W. G. Fateley
Professor R. M. Hammaker
Department of Chemistry
Kansas State University
Manhattan, Kansas 66506

3. INCLUSIVE DATES: 1 June 1978 - 28 February 1981

4. GRANT NUMBER: AFOSR-78-3617

5. COSTS AND FY SOURCE: $40,878, FY78; $40,000, FY80

6. SENIOR RESEARCH PERSONNEL:

A. S. Manocha
D. D. DesMarteau
B. J. Streusand
J. R. Durig
C. J. Marsden
J. D. Witt

7. JUNIOR RESEARCH PERSONNEL

J. J. Blaha
C. E. Meloan
J. C. Kuo

8. PUBLICATIONS:

"Raman Studies of the Adduct Structure of Cl_2 and Br_2 with Piaselenole," J. J. Blaha, W. Brittain, C. E. Meloan, and W. G. Fateley, Applied Spectroscopy, 34, 6, (1980).

"The CF_3 Rotor: Torsional Vibrations for some CF_3OX and CF_3OOX Molecules," R. M. Hammaker, W. G. Fateley, A. S. Monocha, and D. D. DesMarteau, B. J. Streusand, and J. R. Durig, Journal of Raman Spectroscopy, 9, 3 (1980)

"Vibrational Spectra and Normal Coordinate Analysis of CF_3OF and CF_3OCl," J. C. Kuo, D. D. DesMarteau, W. G. Fateley, R. M. Hammaker, C. J. Marsden, and J. D. Witt, Journal of Raman Spectroscopy, 9, 4, (1980).

"Development and Use of Time Resolved Spectroscopy," W. G. Fateley and R. M. Hammaker, Final Technical Report, AFOSR TR-81-0351

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research demonstrated the application of Time Resolved Spectroscopy (TRS) to dynamic conditions in polymers. The Michelson's interferometer and Fourier Transform Spectroscopy (FTS) were employed in this study. TRS technique involves the coordination of reaction stimulation, e.g., pulsed laser excitation of gases or stretching and relaxation in polymers, and the recording of the interferogram at some unit time after stimulation. In the cases of gases, for versatility the reaction vessel is designed to allow either emission or absorption studies. Time resolved spectroscopy provides a very attractive means for the elucidation of the structure of reaction intermediates and products, because this technique provides sufficient data for examination of the band shapes of materials and deduction of the energy distributions within the molecules for successive times during reaction.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Electrochemical Impregnation for the Fabrication of Cadmium Electrodes

2. PRINCIPAL INVESTIGATOR: Dr. Y. K. Kao
Department of Electrical Engineering
University of Cincinnati
Cincinnati, Ohio 45221

3. INCLUSIVE DATES: 15 March 1979 - 30 April 1981

4. GRANT NUMBER: AFOSR-79-0104

5. COSTS AND FY SOURCE: $9,910, FY79 (MINI-GRANT)

6. JUNIOR RESEARCH PERSONNEL: Yung-Chung Lin

7. PUBLICATIONS:

"Electrochemical Impregnation Process in the Manufacturing of Cadmium Electrodes," Yuen-Koh Kao and Yung-Chung Lin, Final Technical Report, AFOSR-TR-81-0617.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research deals with the understanding of the kinetic-process of electrochemical impregnation. A cyclic voltammetric technique was used in a helium atmosphere to study the cathodic deposition of cadmium on nickel. A unique reduction reaction occurs on the nickel electrode in the presence of the cadmium ion. It appears to be the electrodeposition of cadmium oxide which passivates the electrode surface. The electrochemical impregnation process was examined both experimentally and theoretically. Experimentally, two sets of potentiostatic transients were obtained for a nickel microelectrode in two different electrolytes. The first set of data was obtained in an electrolyte which contained no cadmium ion; the second set of data was obtained in an electrolyte which contained cadmium ions. The higher current density obtained in the second data set was due to the occurrence of the co-precipitation reaction between cadmium ions and hydroxy ions which were generated by the electrochemical reaction. Two models, which described the transport process and reactions under two different experimental conditions were developed. The model for a cadmium-ion-free electrolyte was used to identify the rate of the heterogeneous electrode reaction by matching the model prediction with the experimental results. The heterogeneous reaction rate constants so obtained were then used to identify the rate of the homogeneous precipitation reaction by again matching its model prediction with the experimental results.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical Structure by Laser-Produced X-Rays

2. PRINCIPAL INVESTIGATORS: Dr. P. J. Mallozzi
Dr. R. E. Schwerzel
Battelle Memorial Institute
505 King Avenue
Columbia, OH 43201

3. INCLUSIVE DATES: 15 March 1978 - 30 September 1981

4. GRANT NUMBER: AFOSR-78-3575

5. COSTS AND FY SOURCE: $60,090, FY78; $59,798, FY80; $74,750, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. Harold M. Epstein
Dr. B. E. Campbell

7. PUBLICATIONS:

"Laser-EXAFS: Fast Extended X-ray Absorption Fine Structure with a Single Pulse of Laser-Produced X-rays," P. J. Mallozzi, R. E. Schwerzel, H. M. Epstein, B. E. Campbell, Science, 206, 353 (1979).

"Fast EXAFS Spectroscopy with a Laser-Produced X-ray Pulse," P. J. Mallozzi, R. E. Schwerzel, H. M. Epstein, B. E. Campbell, Journal of Applied Physics.

"Laser-Produced Plasmas as an Alternate X-ray Source for Synchrotron Radiation Research and for Microradiography," P. J. Mallozzi, H. M. Epstein, and R. E. Schwerzel, from Advances in X-ray Analysis, 22, Plenum Publishing Company (1979).

"Fast Extended X-ray Absorption Fine Structure Spectroscopy with Laser-Produced X-ray Pulse," P. J. Mallozzi, R. E. Schwerzel, H. M. Epstein, and B. E. Campbell, Physical Review A, 23, No. 2, Feb 1981.

"Flash-EXAFS for Structural Analysis of Transient Species: Rapidly Melting Aluminum," H. M. Epstein, R. E. Schwerzel, P. J. Mallozzi, and B. E. Campbell, Journal of American Chemical Society, 1982.

"Chemical Structure by Laser-Produced X-rays," P. J. Mallozzi and R. E. Schwerzel, Final Technical Report, AFOSR-TR-82-0288.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The technique of Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy is becoming an increasingly important tool for the study of chemical structure in samples which lack long-range order, such as amorphous solids, solutions of biologically important materials, and gases. These studies have gained impetus in recent years by virtue of the availability of synchrotron radiation, which provides a continuous and intense spectrum of the soft X-rays required for EXAFS. A synchrotron, however, is an expensive, cumbersome source of X-rays, to which scientists must travel in order to perform their experiments. A laser X-ray source, on the other hand, is relatively compact, inexpensive, and simple to operate and maintain. Furthermore, there are a variety of novel EXAFS experiments which are inherently beyond the capabilities of synchrotron radiation sources. These experiments, which require short pulse width and intense fluxes of low-energy (< 4 keV) X-rays, are ideally suited to laser-produced X-rays.

In the EXAFS technique, the x-ray absorption coefficient of a material is measured as a function of energy from the K-edge or L-edge of a specific element in the material to as far as 1000 electron volts above the edge. The absorption of x-rays by the element is accompanied by the ejection of photoelectrons, which can be scattered from neighboring atoms. Back-scattering of these photoelectrons from atoms in the immediate vicinity of the absorbing atom gives rise to a periodic "wiggle" structure in the x-ray absorption spectrum. By analyzing this "wiggle" structure above the absorption edge of a particular element, information can be obtained about the spatial arrangement of atoms in the immediate vicinity of the absorbing species. Since only the nearby atoms are involved, long-range order is not required; therefore, the EXAFS technique can be applied to the study of a broad class of materials.

The overall objective of this research was two-fold. The first was to extend the range and accuracy of laser-EXAFS measurements beyond the present state of the art. The second was to use the unique characteristics of laser-produced x-rays to perform experiments which could not easily be performed with synchrotron x-ray sources. The early experiments showed that it is possible to obtain well-resolved EXAFS spectra of light elements (atomic numbers ranging up to 40) with a single nanosecond pulse of soft x-rays produced with neodymium-doped-glass laser. EXAFS spectra of both aluminum and magnesium were measured with nanosecond pulse. It was also found that 10-10 joule laser pulses would suffice instead of the 100 joule laser-pulse. The measuring time evolution of chemical structure by laser-EXAFS was also tested.

This represents a dramatic improvement in the speed and ease of obtaining EXAFS data compared to what is possible with other known x-ray sources. The technique also makes possible the measurement of "flash-EXAFS" spectra of transient species having lifetimes of a few nanoseconds or less. Thus, with this technique it may soon be possible to make "snapshots" or "movies" of the structural changes that occur in molecules when they are excited by optical or other means. This capability is provided almost automatically by the pulsed nature of the laser-EXAFS measurement.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: New Solid Superionic Conductors Containing Cu^+, Ga^+, In^+ and Tl^+

2. PRINCIPAL INVESTIGATORS: Dr. Duward F. Shriver
Department of Chemistry
Dr. Donald H. Whitmore
Department of Materials Science and Engineering
Northwestern University
Evanston, IL 60201

3. INCLUSIVE DATES: 1 January 1977 - 30 September 1981

4. GRANT NUMBER: AFOSR-77-3227

5. COSTS AND FY SOURCE: \$50,000, FY77; \$50,000, FY78; \$92,253, FY79;
NO-COST EXTENSION 1 Oct 80 - 30 Sep 81

6. JUNIOR RESEARCH PERSONNEL:

Carol Chaney
R. Ammlung
M. Savarese
B. Papke
R. Dupon
A. Herlihy
T. Prichett
A. Pechenik

7. PUBLICATIONS:

"Trends in Heavy-Metal Solid State Ionic Conductors: A Comparison of Cu^+, Ag^+, In^+, and Tl^+ Transport," R. L. Ammlung, R. P. Scaringe, J. A. Ibers, D. F. Shriver, and D. H. Whitmore, J. Solid State Chem., 29, 401 (1979).

"Indium(I) and Thallium(I) Transport in Halide Lattices," D. F. Shriver, M. A. Ratner, R. Ammlung, J. I. McOmber, and D. H. Whitmore, Proc. Int. Conf. on Fast Ion Transport in Solids, ed. by P. Vashishta, J. N. Mundy and G. K. Shenoy (Amsterdam: North-Holland, 1979), p. 515.

"Ab-Initio Electronic Structure Studies of Mobility Paths in Fast Ion Conductors. I.," J. I. McOmber, S. Topiol, M. A. Ratner, D. F. Shriver, and J. Moskowitz, J. Phys. Chem. Solids, 41, 447 (1980).

"Polarization Study on the Solid Electrolyte $Cu_{16}Rb_4I_{7+x}Cl_{20-(7+x)}$ ($0 \lesssim x \lesssim 1$)," C. Chaney, D. F. Shriver, and D. H. Whitmore, Solid State Ionics, 5, 505 (1981).

"Vibrational Spectroscopy and Structure of Polymer Electrolytes, Poly(ethylene Oxide) Complexes of Alkali Metal Salts," B. L. Papke, M. A. Ratner, and D. F. Shriver, J. Phys. Chem. Solids, 42, 493 (1981).

"Synthesis and Properties of Fast Ion Conductors of the Heavy Metal Halide Compounds of Monopositive Metal Ions," Ph.D. Thesis: R. L. Ammlung, Northwestern University, 1979.

"Vibrational Spectroscopic and Theoretical Investigations of Heavy Metal Halide Fast Ion Conductors," Ph.D. Thesis: J. I. McOmber, Northwestern University, 1981. (The expenses for theoretical calculations associated with this research were largely supported from AFOSR funds.)

"Vibrational Spectroscopy, Structure, and Ion Transport in Complexes of Poly(ethylene oxide) with Alkali Metal Salts: A Class of Polymeric Solid Electrolytes," Ph.D. Thesis: B. L. Papke, Northwestern University, 1982. (Thesis defended in 1981)

"Ionic and Electronic Conduction Processes in the Solid Electrolyte $Cu_{16}Rb_4I_{7+x}Cl_{20-(7+x)}$ $(0 \lesssim x \lesssim 1)$," Ph.D. Thesis: C. Chaney, Northwestern University, 1982.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The present emphasis in advanced electronic instrumentation is towards greater miniaturization. As a result of this trend, there has been a rapidly growing interest in, and demand for, solid electrolytes suitable for low-power, long-lifetime, miniaturized battery systems. The main drawback, thus far, to the use of solid electrolytes in such miniaturized cells has been their high cost (in the case of the silver ion-conducting electrolytes) or a high internal resistance, associated with a low specific conductivity (in the case of solid electrolytes containing mobile ion species other than silver). The overall objectives of this study included: (1) the synthesis of new solid electrolyte materials which differ in composition and mobile ion from those currently available, with special emphasis on complex salts containing mobile Cu(I), Ga(I), In(I), and Th(I) ions, (2) the screening of new solid materials for high ionic conductivity coupled with low electronic conductivity; and (3) detailed characterization studies of the new solid electrolyte materials which were aimed at developing an understanding of charged particle transport and the effects of temperature and impurities on transport properties.

In order to develop a deeper understanding of the role of electronic structure of the cation on fast ion transport in solids, we investigated a series of solid electrolytes of the formula A_2MX_4 ($A^+ = Cu^+$, Ag^+, In^+, or Tl^+; $M^{2+} = Zn^{2+}$, Cd^{2+}, or Hg^{2+}; $X + Br^-$ or I^-). Electrical measurements on these materials show consistently lower conductivity for the $d^{10}s^2$ ions, In^+ and Tl^+, than for the d^{10} ions, Cu^+ and Ag^+. A single crystal x-ray investigation of the structure for Tl_2ZnI_4 demonstrates that the cation resides in a low symmetry 7-coordinate environment. Raman spectroscopy and x-ray powder diffraction suggest a similar structure for the corresponding In^+ salt. By contrast, structural data in the literature indicate that Cu^+ and Ag^+ reside in tetrahedral sites in their respective compounds. These comparisons suggest that the lower conductivity of the $d^{10}s^2$ ions arise from the structural differences. The structural differences are imposed by the unsymmetrical polarization of the $d^{10}s^2$ ions which contrasts with the symmetrical polarization of d^{10} ions.

The possibility was also considered that difference in electronic structure of the cation might influence the energy of the transition state for ion transport. To address this issue, Ab initio Hartree-Fock LCAO-MO calculations were performed on MI_4 arrays. The ground state structure was taken as the cation residing in the center of a tetrahedral I_4 array and the transition state was modeled by the ion in the face of the I_4 array. Lower energies were found for the movement of the d^{10} ions into the face of the iodide tetrahedron. In a classical sense this result arises from the energetically favorable quadrupolar polarization of the d^{10} ions which lowers the energy of the local D_{3h} symmetry MI_4 array for the cation in the tetrahedral face. The $d^{10}s^2$ ions on the other hand are most susceptible to dipolar polarization, which is not compatible with D_{3h} local symmetry.

These results demonstrate that the detailed electronic structure of the cation can have a profound influence on ion transport. Furthermore, the results indicate that the low mobility of the group III monopositive ions results from the fundamental general causes and therefore these ions are not attractive for further exploration as mobile species in solid electrolytes.

The best solid copper ion conductors known to date are the compounds $Cu_{16}Rb_4Cl_{13}I_7$ and $Cu_{16}Rb_4Cl_{12}I_8$; these possess ionic conductivities at 25°C of 0.34 $(\Omega\ cm)^{-1}$ and 0.44 $(\Omega\ cm)^{-1}$ and activation energies of 0.07 and 0.15 eV, respectively. However, for these materials to be useful as solid electrolytes in commercial primary cells, they must also exhibit negligibly small specific electronic conductivities. Measurements of the electronic conductivities of these copper ion salt were made with the aid of a d.c. polarization technique. The concentrations of electron holes in these materials were determined as a function of temperature from an analysis of transient currents in such polarization cells. The specific conductivity for the electron holes exhibited an activation energy of 1 eV and a room-temperature value of $5 \times 10^{-16} (\Omega\ cm)^{-1}$. The hole concentrations ranged from 10^9 cm^{-3} at 25°C to 10^{11} cm^{-3} at 130°C, and the transport number for the electron holes ranged from 10^{-15} at 25°C to 10^{-11} at 140°C. Since the partial electron hole conductivities and transport numbers are negligibly small at all temperatures where these phases are solids and their Cu^+ ion conductivities are outstanding, these compounds should be excellent solid electrolytes in commercial primary cell applications.

A new research effort in polymer electrolytes was launched under AFOSR support. The specific systems studied have the approximate composition MX·4PEO (M is an alkali metal ion, X is a large anion, and PEO is the repeat unit of polyethylene oxide). These are promising materials for application in solid state electrochemical devices. In contrast to inorganic electrolytes, the highly compliant polymer electrolyte should maintain good contact with the electrode materials.

In order to understand the structures and dynamics of these materials detailed infrared and Raman spectroscopic investigations were performed. Mid-infrared spectra provided information on the conformation of the polymer backbone, and high frequency Raman data indicated the polymer is wrapped around the cations. Far-infrared spectra reveal the presence of cation translational modes for which the frequencies scale approximately as the square root of the mass of the cation and which have negligible dependence on the nature of the anion. These results, along with the published x-ray fiber repeat distances and steric considerations, are best fit by a model in which the cations reside inside helical spirals of the polymer. The anions are thought to reside outside of these helices.

AFOSR Program Manager: Denton W. Elliott

COMPLETED PROJECT SUMMARY

1. TITLE: Lithium Based Anodes for Solid State Batteries

2. PRINCIPAL INVESTIGATOR: Professor B. C. H. Steele
Department of Metallurgy & Materials Science
Imperial College
London, SW7 2BP UK

3. INCLUSIVE DATES: 30 September 1977 - 30 September 1980

4. GRANT NUMBER: AFOSR-77-3460

5. COSTS AND FY SOURCE: $17,220, FY77; $24,984, FY78; $30,463, FY80

6. SENIOR RESEARCH PERSONNEL:

R. A. H. Edwards
J. R. Owen

7. PUBLICATIONS:

"Lithium Based Anodes for Solid State Batteries," B. C. H. Steele, Final Report, AFOSR-TR-81-0652.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A considerable effort has been devoted to the production of a rechargeable lithium anode for use in secondary lithium batteries. Three main problems associated with the use of pure lithium as the negative plate are as follows: (a) the formation of surface films with excessive resistance, (b) the isolation of redeposited lithium particles, and (c) the lithium dendrite cell shorting. Preliminary investigations involved the synthesis of lithium based anodes $Li_x Mn_4 P_4$ and Li-Fe-Si alloys. These materials exhibited promising thermodynamic and transport properties. The technique selected to measure these properties over a wide composition range involved the use of a "Staircase wave cyclic voltammetry." This technique was applied to the compounds of iron, silicon, a glassy metal of iron, silicon, boron composition and a newly found prospective negative plate material of mercury-lithium. An analysis of composite elctrodes - those containing an additional ionic conductor, e.g., a solid electrolyte, as the grain boundary phase of the charge storage material showed that the criteria initially applied to the selection of an electrode may be significantly relaxed. Experiments with the composite of lithium-aluminum alloy with the solid electrolyte polyethylene oxide-lithium trifluoromethane sulphonate have verified the analysis which can be applied to many more systems.

AFOSR Program Manager: Denton W. Elliott

SURFACE CHEMICAL RESEARCH AT AFOSR

Capt Lee E. Myers

An appraisal of Air Force short, medium, and long-term surface material needs has resulted in significant changes in the surface chemistry research program. Emphasis will be placed on the molecular interpretation underlying the surface phenomena. As in the past, the investment will bear upon areas of specific Air Force interest. The dominant topic will be in surface reactions/reactivity. This program emphasizes both corrosive and non-corrosive type surface reactions with a small amount of support for analytical technique development. The presently supported areas of lubrication and adhesion chemistry will be replaced with efforts in the surface chemistry of thin films and electromagnetic materials.

Each of these programs will be briefly outlined below.

As stated, the largest surface chemistry program will remain in the area of surface reactions/reactivity. This research task will encompass work in a wide variety of surface specialties including gas/surface interactions, including chemical and physical adsorption, diffusion and desorption studies; surface characterization, with emphasis upon structure/reactivity correlation; and surface reaction kinetics and mechanism. The only programmed restriction applied to this research area is the omission of solar and petroleum related surface catalytic chemistry. Scientific quality and uniqueness will remain as essential factors for evaluation of proposals in the area.

Thin films are involved in many aspects of the high technology of today. One significant Air Force application of this technology is in high energy laser optical coatings. Emphasis will be placed upon the fundamental understanding of various aspects of thin film science including film characterization, gas/thin film interaction and reactivity, substrate/thin film stability, film nucleation and growth, and intense light/thin film interactions. Being a new program interest, areas of emphasis should be expected to be refined and focused over the coming years.

The third and final program area in surface chemistry is that of electromagnetic materials. This topic is of general interest to the Air Force, as it is to many other technology user groups. The AFOSR effort in chemistry will not be directed at the engineering of smaller, faster electronic devices and sensors but rather at consideration of the fundamental surface chemical questions involved in the specialized world of electromagnetic materials. Of particular interest is the problem of probing the microscopic chemical behavior of solid/solid interfaces and properties of multiple thin layers. Emphasis will be placed upon radical or new concepts for the understanding of this important class of materials. As with the thin film program, this program can be expected to modify and focus its interests during its initial years.

A new occurrence this year for the surface program has been participation in the annual molecular dynamics contractors' meeting. It is planned that each contractor and grant recipient in the surface chemistry program will have the opportunity to present results at this meeting on alternating years. This co-program is expected to become a permanent event for the AFOSR molecular dynamic and surface chemistry programs.

In conclusion I'd like to reiterate the recent changes in the AFOSR surface chemistry program. Although lubrication and adhesion surface chemistry are presently being phased out, new research areas in thin films and electromagnetic materials are being opened. Vital and exciting research opportunities exist in both of these areas for fundamental surface chemistry projects. It is expected that these programs along with surface reactions/reactivity will continue to grow over the next several years.

COMPLETED PROJECT SUMMARY

1. TITLE: Effects of Surface Morphology and Chemical Composition on the Durability of Adhesively Bonded Aluminum Structures

2. PRINCIPAL INVESTIGATOR: Dr. G. D. Davis (T. S. Sun)
Martin Marietta Corporation
Martin Marietta Laboratories
1450 South Rolling Road
Baltimore, MD 21227

3. INCLUSIVE DATES: 15 July 1978 - 14 July 1981

4. CONTRACT NUMBER: F49620-78-C-0097

5. COSTS AND FY SOURCE: $12,500, FY78; $50,820, FY79; $50,596, FY80; $52,392, FY81

6. SENIOR RESEARCH PERSONNEL:

J. D. Venables	J. S. Ahearn
J. M. Chen	B. M. Ditchek

7. JUNIOR RESEARCH PERSONNEL

D. K. McNamara
C. Froede
R. Hopping

8. PUBLICATIONS:

"Characterization of Aluminum Surfaces Prepared for Adhesive Bonding," J. D. Venables, D. K. McNamara, J. S. Sun, R. L. Hopping, B. Ditchek, and J. M. Chen, Proceedings of Structural Adhesive and Bonding Conference, El Segunda, CA (March 1979).

"Interpretation of AES Depth Profiles of Porous Al Anodic Oxides," T. S. Sun, D. K. McNamara, J. S. Ahearn, J. M. Chen, B. Ditchek, and J. D. Venables, Applications of Surface Science, 5, 406 (1980).

"Development of Oxide Films on Al with the Phosphonic Acid Anodization Process," J. S. Ahearn, T. S. Sun, J. D. Venables, C. Froede, and R. Hopping, Proceedings of SAMPE/ASM Conference, Los Angeles, CA (February 1980).

"Correlation of Surface Chemistry and Durability of Aluminum/Polymer Bonds," J. S. Ahearn, G. D. Davis, T. S. Sun, and J. D. Venables, Proceedings of Symposium on Adhesion Aspects of Polymeric Coatings, Minneapolis, Minnesota (May 1981).

"Application of Surface Behavior Diagrams to the Study of Hydration of Phosphoric-Acid-Anodized Aluminum," to be published in the Journal of Materials Science.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The hydration of aluminum surfaces prepared for adhesive bonding by anodization in phosphoric acid has been studied using surface behavior diagrams. These surface behavior diagrams, which are similar to phase diagrams for equilibrium bulk phases, trace the evolution of the aluminum adherend surface composition, obtained by X-ray photoelectron spectroscopy, during the hydration process. When supplemented with high resolution scanning electron micrographs and Auger depth profiles, the surface behavior diagrams show that hydration proceeds in three steps. The first is reversible and consists of the adsorbption of water by the monolayer of AlPO4 initially present on the surface. It involves no change in the oxide morphology. The second, which appears to be rate controlling, involves the slow dissolution of the phosphate followed by rapid hydration of the exposed alumina to the oxyhydroxide, boehmite. During this stage, extensive morphological changes occur as the boehmite fills the pore cells and bridges the whiskers of the original surface. The final step consists of the nucleation and growth of the trihydroxide, bayerite, on top of the boehmite. Using these results as examples, we propose the surface behavior diagram approach as a new tool for the study of surface reactions in general.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Analysis of Lubricant Films in Bearings under Incipient Failure Conditions

2. PRINCIPAL INVESTIGATOR: Dr. James L. Lauer
Department of Mechanical Engineering
Aeronautical Engineering & Mechanics
Rensselaer Polytechnic Institute
Troy, NY 12181

3. INCLUSIVE DATES: 1 January 1978 - 30 June 1981

4. GRANT NUMBER: AFOSR-78-3473

5. COSTS AND FY SOURCE: $51,000, FY78; $55,000, FY79; $65,157, FY80

6. PUBLICATIONS:

"Polarized Infrared Emission Spectra from Operating Bearings," James L. Lauer, Paper No. 592. Invited paper presented at the Coblentz Symposium of the 29th Pittsburgh Conference at Cleveland, Ohio, March 1, 1978.

"Chemistry and Physics of Lubricants," James L. Lauer. One-hour invited lecture at Session III - Lubricants, Manufacturing of Wire III, Clinic, Society of Manufacturing Engineers, April 5, 1978, in Newark, New Jersey. Published in Wire World, 1978.

"Study of Polyphenyl Ether Fluid (5P4E) in Operating Elastohydrodynamic Contacts by Infrared Emission Spectroscopy," James L. Lauer. Presented at the ASLE/ASME Joint Lubrication Conference in Minneapolis on October 25, 1978 (Paper No. 78 - Lub-21).

"High-Pressure Infrared Interferometry," James L. Lauer, in Fourier Transform Infrared Spectroscopy, Vol. 1, Chapter 5, pp. 169-218, Academic Press, New York 1978.

"Traction and Lubricant Film Temperature as Related to the Glass Transition Temperature and Solidification," James L. Lauer, ASLE Transactions, 21, 250-256 (July 1978).

"Orientation of Lubricant Molecules in Operating Bearings by Polarized Infrared Fourier Microspectroscopy," James L. Lauer and Vincent W. King, Paper No. 70. Presented at the 25th Canadian Spectroscopy Symposium, Mt. Gabriel, Quebec, Canada, September 28-29, 1978.

"Fourier Emission Infrared Microspectrometer for Surface Analysis," James L. Lauer and Vincent W. King, Paper No. 17. Presented at the 25th Canadian Spectroscopy Symposium, Mt. Gabriel, Quebec, Canada, September 28-29, 1978.

"Study of Polyphenyl Ether Fluid (5P4E) in Operating Elastohydrodynamic Contacts by Infrared Emission Spectroscopy," James L. Lauer and Vincent W. King, J. Lubrication Technology, 101, 67-73 (1979).

"Discussion of Paper by Bair, S. S. and Winder, W. O., "Shear Strength Measurements of Lubricants at High Pressure," James L. Lauer, J. Lubrication Technology, 101, 256 (1979).

"Conditions of Lubricants in Operating Elastohydrodynamic Bearing Contacts by Simultaneous Infrared Emission Spectrophotometry," James L. Lauer and Vincent W. King. Presented at the Second International Conference on Infrared Physics, EHD Zurich, Switzerland, March 5-9, 1979. Proceedings of the Second International Conference on Infrared Physics, pp. 379-390, 1979.

"Fourier Emission Infrared Microspectrophotometer for Surface Analysis - I. Application to Lubrication Problems," James L. Lauer and Vincent W. King, Infrared Physics, 19, 395-412 (1979).

"Spectroscopic Study of the Effect of an EHD Contact of Trichloroethane Addition to a Traction Fluid," James L. Lauer and Vincent W. King. Paper presented at the Annual ASLE Meeting in Anaheim, May 1980. (Preprint No. 80-AM-4D-2).

"Temperature Gradients through EHD Films and Molecular Alignment Evidenced by Infrared Spectroscopy," James L. Lauer and Vincent King. Paper presented at the ASLE Joint Lubrication Conference, San Francisco, August 1980. (Preprint No. 80-C2/Lub-12).

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"Emission Spectra from Operating Bearings," James L. Lauer. Seminar lecture, Department of Mechanical Engineering, Aeronautical Engineering and Mechanics, RPI, December 3, 1980.

"Friction Polymers and Other Chemical and Physical Phenomena at Lubricant Boundaries," James L. Lauer. Critical Review Presented at the "Interdisciplinary Collaboration in Tribology (ICT)" Meeting, NASA/LeRC, Cleveland, Ohio, March 2, 1981.

"Analysis of Lubricants by Infrared Fourier Emission Spectrophotometry," James L. Lauer. Inorganic/Analytical Chemistry Seminar Lecture at RPI on February 26, 1981.

"Polarized Infrared Emission Spectra of Materials Adsorbed on Solid Surfaces," James L. Lauer and L. E. Keller. Paper No. 145, presented at the 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Atlantic City, New Jersey, March 9, 1981 and published in the Proceedings.

"Temperature Gradients through EHD Films and Molecular Alignment Evidenced by Infrared Spectroscopy," James L. Lauer and Vincent W. King, ASME Trans., J. Lubr. Tech., 103, 65-73 (January 1981).

"Spectroscopic Study of the Effect on an EHD Contact of Trichloroethane Addition to a Traction Fluid," James L. Lauer and Vincent W. King, ASLE Transactions, 24, 3, 331-339 (1981).

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"Microscopic Contour Changes of Tribological Surfaces by Chemical and Mechanical Action," James L. Lauer, Simon Fung and P. Kwan. Offered for presented at the ASME/ASLE Lubrication Conference, Washington, D.C., October 5-7, 1982.

"Infrared Emission Spectra, Traction and Thickness of EHD Films Bounded by TiN-Coated Steel," James L. Lauer, P. Vogel and L. E. Keller. Offered for presentation at the ASME/ASLE Lubrication Conference, Washington, D.C., October 5-7, 1982.

"Phenomena at Moving Phase Boundaries." Invited speaker (J.L. Lauer) at the 1982 Gordon Research Conference on Friction and Lubrication.

RPI Patent Case No. 198, "Method for the Detection and Analysis of Oriented Material," L. E. Keller, J. L. Lauer and V. W. King. Assigned to the Secretary of the Air Force, October 1981.

RPI Patent Case No. 199, "Adjustable Compact Radiation Source with Controllable Outer Surface Temperature," L. E. Keller and J. L. Lauer. Assigned to the Secretary of the Air Force, October 1981.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Since infrared emission microspectrophotometry is capable of the analysis of the extremely thin films between surfaces of operating, highly loaded bearings, it was called on to help understand the phenomenon of scuffing, which often leads to sudden and catastrophic failure of moving parts in advanced aircraft.

New very sophisticated and extremely sensitive apparatus, a Fourier emission microspectrophotometer, was constructed.

Two instances of failure were studied spectroscopically, one with a cycloparaffinic lubricant, one with an aromatic lubricant. Apparently both were triggered by the presence of an organic chloride under very severe operating conditions: elastohydrodynamic regime, shear rates near 10^6 sec $^{-1}$, non-conforming bearing surfaces, very high loads. Ferric chloride could have catalyzed the reactions leading to polymerization and carbonization of the lubricant by ionic mechanisms well understood by catalytic workers. The temperatures accompanying the failure mechanism--which, of course, led to contact between moving surfaces with possible welding and contact breaking--were very much higher than even the high temperatures expected for this type of operation. It is therefore possible that water and oxygen, which are very likely present in the lubricant, in small concentrations, were effectively squeezed out, thus making the ionic reactions possible.

Since these failures could be followed spectroscopically, at least to some extent, it does seem likely that metal/metal contact started the process. However, some metal/metal asperities contact has been shown to always be present under elastohydrodynamic conditions. The key to the avoidance of failure is a healing process, by which the asperities making contact are worn off before they can cause failure. When the chloride was present this mechanism was interfered with. Reasoning by an analogy with electrical contacts, where organic chlorides and other halides are deliberately sprayed on to make contact, the key to the mechanism could be the presence of a thin oxide layer on the metal surface. Interestingly, titanium nitride-coated bearings never scuffed, although by compaison to stainless steel our experience has been very limited.

It would seem to be almost impossible to avoid the presence of chlorides almost entirely. However, their concentration could be kept low and other additives could be used to advantage in counteracting them. The observation that an organic chloride could come out of solution under elastohydrodynamic pressure and then accumulate in the contact region could mean that a "solubilizing" agent could be useful. The literature is full of "solubilizers" to keep oil in aqueous suspension, but almost blank for nonaqueous solvents. A study along these directions could be fruitful.

Related to this idea is the observation of flow dichroism resulting from molecular orientation undergone by every fluid looked at. By this mechanism fluid viscosity can be significantly decreased. The lubricating gap is thereby reduced and failure made more likely. Since the orientation must occur in the inlet zone of the contact, fluids that would be expected to orient with difficulty would have an advantage. Indeed long chain molecular species seem to be very superior lubricants.

In addition to the above conclusions the work has been most useful by helping in the development of apparatus for the study of thin layers on solid surfaces by infrared emission microspectrophotometry. By picking up the radiation emitted from a very small area (i) blackbody radiation and intergranular scattering is much reduced and (ii) radiation originating from transition moments normal to the surface can still be observed. All-reflecting objective lenses of high numerical aperture are needed to introduce the radiation into an already very sensitive Fourier spectrometer of high optical speed. The spectral contrast can be enhanced further by differential point by point recording. In one mode of operation the source radiation is compared to a blackbody reference exactly controlled at the sample temperature and flux level and in another mode use is made of the fact that most thin surface layers are oriented and therefore polarized, and a continuous differencing process between signals of two mutually perpendicular polarization planes is carried out. The latter procedure, as it discriminates against randomly polarized stray graybody radiation, would seem to be sensitive enough to allow the analysis of monomolecular layers. These procedures have already been used advantageously in the analysis of various Air Force problems.

AFOSR Program Manager: Lee E. Myers, Capt, USAF

POLYMER SCIENCE

Dr. Donald R. Ulrich

The Air Force polymer science program has focused on the development of new processible, high performance materials for structural application in aeronautical, missile, and space missions. The uniqueness for scientific and practical advancement has arisen from imaginative concepts for new materials derived from an understanding of the interaction of structure, processing and properties. Two achievements embodying these concepts--ordered polymers and polymeric alloys--are described.

Ordered Polymers - An Advanced Concept in composite Materials

The Air Force Office of Scientific Research and Air Force Wright Aeronautical Laboratory/Materials Laboratory (Dr. Thaddeus Helkminiak) are coinducting a research program to develop self-reinforced or ordered polymers. The goal is the attainment of mechanical properties and environmental resistance from polymers which are compatible with those now being obtained from fiber-reinforced composites, but without the use of fiber reinforcement.

As a corporate program, basic research has been performed by SRI International, AFWAL/ML in-house, Stanford University, Carnegie-Mellon University, University of Cincinnati, University of Virginia, Texas A&M, Texas Tech, and University of Dayton Research Institute. Exploratory research is being conducted in-house at AFWAL/ML and by University of Massachusetts, Celanese Corporation, SRI International, and Carnegie-Mellon University.

The program has developed the ordered polymer polybenzothiazole (PBT). This polymer has extended rigid chain alignment rather than the flexible chains of resins employed as matrices and requiring reinforcement in graphite/epoxy and other composites. (Figure 1) As a result, PBT has superior tensile strength and ultra high modulus as well as excellent thermal stability and environmental resistance in comparison with aramids, other polymers, and carbon, glass and steel fibers. During FY 80 the modulus was increased from 25 to 45 x 10^6 psi and the strength from 200,000 to 400,000 psi. These excellent mechanical properties are retained at elevated temperature. (Figure 2)

The first spinoff of the ordered polymer research program occurred during FY 81 with the transition to development of polybenzothiazole fiber. Basic research advances in fiber scale up chemistry have enabled PBT engineering materials to be produced during FY 81 with the same excellent properties reported during FY 80 for PBT research fibers. (Figure 2). The combination of new techniques to obtain very pure PBT monomer on a large scale and to synthesize high yields of high molecular weight PBT

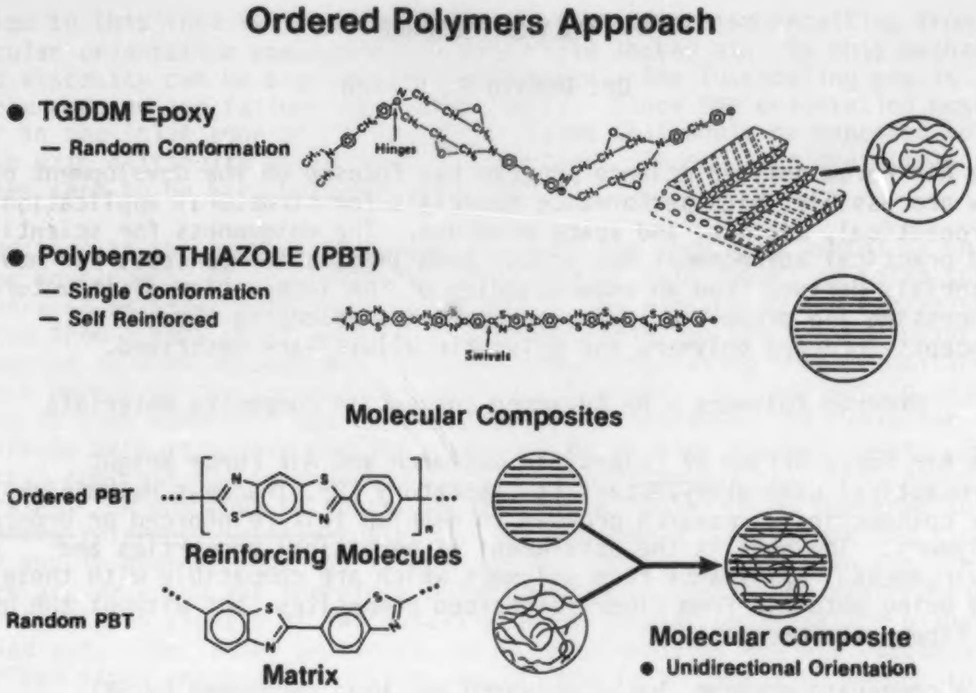
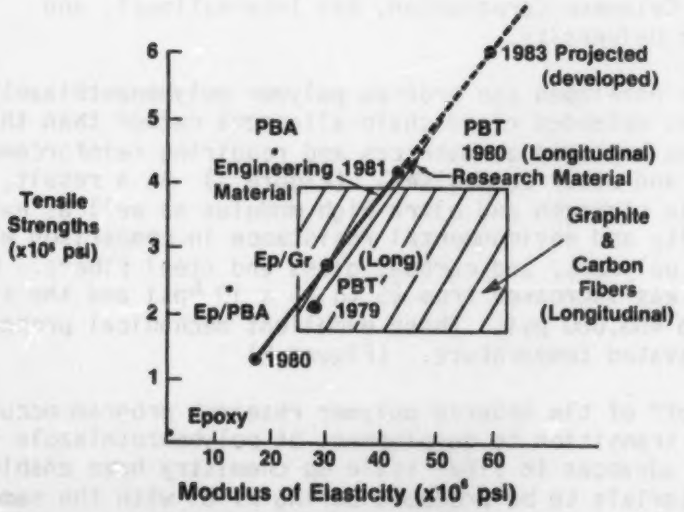

Ordered Polymers Approach
● TGDDM Epoxy
— Random Conformation
Hinges
● Polybenzo THIAZOLE (PBT)
— Single Conformation
— Self Reinforced
Swivels
Molecular Composites
Ordered PBT
N
S
n
Reinforcing Molecules
Random PBT
Matrix
Molecular Composite
● Unidirectional Orientation

FIGURE 1



- **High Tensile Strength**
- **High Modulus of Elasticity**
- **Good Thermal Environment Properties**
- **Thermal Retention of Mechanical Properties**

FIGURE 2

polymer has resulted in ten pound lot production of polymer. Fibers produced from these lots in quantity have a reproducible strength of 400,000 psi, an ultra high modulus of 45×10^6 psi and excellent thermal and environmental stability.

During FY 81 the Air Force Wright Aeronautical Laboratory/Materials Laboratory transitioned this fiber research into two development contracts with DuPont and Celanese for the scale up and quantity production of PBT fibers. Acceleration of these programs to provide large quantities of PBT fiber for demonstration projects is under consideration by the Defense Advanced Research Projects Agency. The outstanding mechanical and thermal properties of processible PBT will provide a new high performance lightweight structural material for missile, spacecraft, and aircraft applications.

Current and future research in the ordered polymer research program is emphasizing the processing of PBT films and laminates with excellent mechanical properties and environmental stabilitry, bulk structures of PBT self-reinforced molecular composites, and electrically conductive PBT. In the molecular composite concept rigid chain PBT acts as reinforcement for flexible chain PBT much like chopped fibers reinforce a resin matrix. The molecular composites are expected to have the excellent mechanical properties, thermal stability and environmental resistance of PBT without the cost, fabrication problems, and delamination problems of fiber reinforced composites.

Polymer Alloys

Molecular level alloying in polymers has been achieved for the first time. This has resulted in significant improvements in the tensile strength, optical transparency, and use temperature of polymer sheets and films. Alloying on the molecular scale has been verified with a new low frequency application of laser Raman spectroscopy. (Figure 3).

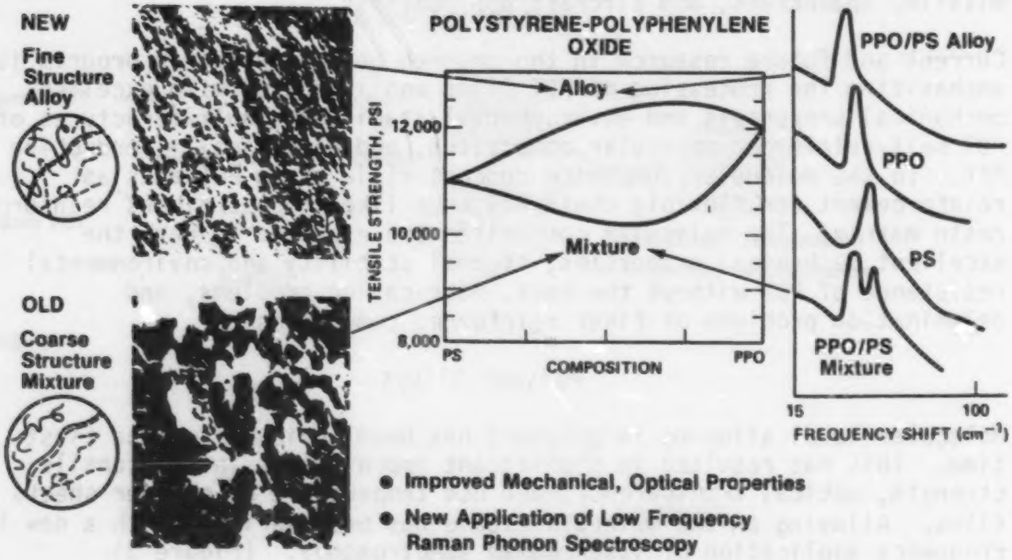
Generally at ambient temperatures two polymer systems are incompatible. They will mix only by agitation, forming inhomogeneous mixtures with course structures. This results in films and sheets with poor mechanical integrity and low optical quality. Through molecular modification the incompatible two phase regime can be shifted to a high temperature regime. A new phenomenon in polymers, this allows a single, stable phase to exist at ambient temperatures. Low temperature thermal annealing then leads to a fine, homogeneous structure.

This is illustrated with the polyphenylene oxide-polychlorostyrene system by transmission electron microscopy at the highest magnification (20 Angstrom field of view). The frequency shift shown by laser Raman spectroscopy at low frequency delineates the molecular level miscibility. Such information is not readily available from optical or X-ray methods which provide information on a space averaged structure.

Future research will investigate the control and compatibility of ultrastructural level features - those at the 10-1000 Angstrom level which can be developed in polymer alloys and the effect on mechanical and electromagnetic properties.

This research has been performed by the University of Massachusetts and the State University of New York at Buffalo.

Molecular Level Polymer Alloys



- Improved Mechanical, Optical Properties
- New Application of Low Frequency Raman Phonon Spectroscopy
  — Molecular Level Alloying

FIGURE 3

COMPLETED PROJECT SUMMARY

1. TITLE: Light Scattering from Macromolecular Systems - Molecular Crystals and Polymers

2. PRINCIPAL INVESTIGATOR: Dr. Elliot R. Bernstein
Department of Chemistry
Colorado State University
Fort Collins, CO 80523

3. INCLUSIVE DATES: 1 June 1977 - 30 September 1981

4. GRANT NUMBER: AFOSR-77-3317

5. COSTS AND FY SOURCE: \$45,269, FY77; \$46,258, FY78; \$62,000, FY79; \$85,407, FY80

6. SENIOR RESEARCH PERSONNEL: Dr. H. Yusada

7. ASSOCIATE RESEARCH PERSONNEL:

Dr. B. B. Lal
Dr. K. M. Chen
Dr. G-J. Wu
Dr. A. Yoshihara
Dr. C. L. Pan

8. JUNIOR RESEARCH PERSONNEL: T. Lewis

9. PUBLICATIONS:

"Light Scattering from Macromolecular Systems - Molecular Crystals and Polymers," E. Bernstein, Final Report, AFOSR-77-3317, November 1981.

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"Structural Transition and Elastic Anomalies in S-Triazine, $C_3N_3H_3$," J. C. Raich, E. R. Bernstein, and A. Yoshihara, Chem. Phys. Lett., 82, 138 (1981).

"On the Phase Transition in Benzil," A. Yoshihara, W. D. Wilber, E. R. Bernstein, and J. C. Raich, J. Chem. Phys., submitted.

"Theory of Structural Transformations in Orientationally Disordered Crystals," J. C. Raich, E. R. Bernstein, and A. Yoshihara, Trans. Am. Cryst. Assoc., 17, 1 (1981).

"Light Scattering Study of the Phase Transition in Sym-Triazine," A. Yoshihara, J. C. Raich, and E. R. Bernstein, J. Chem. Phys., submitted.

"Critical Behavior in Annealed and Unannealed Benzil Crystals," A. Yoshihara, J. C. Raich, and E. R. Bernstein, J. Chem. Phys., submitted.

"Comment on the Quasi-Harmonic Treatment of the Structural Phase Change in S-Triazine," J. C. Raich and E. R. Bernstein, J. Chem. Phys., submitted.

"On the Phase Transition in Chloranil," E. R. Bernstein, A. Yoshihara, and J. C. Raich, J. Chem. Phys., to be submitted.

"Phase Transitions in a Lyotropic Liquid Crystal, E. R. Bernstein, G-J. Wu, and A. Yoshihara, J. Chem. Phys., to be submitted.

10. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of this research have been to:

A. Characterize phase transitions theoretically and experimentally in molecular crystal systems;

B. Apply aforementioned understanding gained by light scattering studies and theoretical interpretation to the more complex system of lyotropic liquid crystals; and

C. Apply the knowledge gained on the model systems of increasing complexity to polymer liquid crystals and solid polymers as observed by laser light scattering techniques.

Experimentally, a novel and unique apparatus has been constructed to measure light scattering from crystal, liquid crystal, and polymer samples. This system has a frequency range for low frequency motion in the samples between 10^6 and 1 Hz as well as 30 GHz and 100 MHz. Both Brillouin and correlation spectra have been observed and studied from triazine, trioxane, chloranil, benzil, a lyotropic liquid crystal and various ordered polymer samples. Theoretically, a number of calculations and descriptions of phase transition and critical phenomena of various types have been generated.

A mean field thermodynamic theory to treat the results in triozane, triazine, benzil and chloranil have been developed, which are not based on critical fluctuations. Equations of motion techniques have been used to present discussions of critical behavior observed in triazine, chloranil, and benzil.

Benzil is a particularly interesting system in terms of more complex polymeric systems. It evidences defect dominated light scattering, correlation behavior, and critical phenomena. It also responds to external stress with a critical correlation function. All of these phenomena have been modeled and explained using the theory of inelastic solids. This is an important finding and treatment because of its application to polymeric systems.

Studies of lyotropic liquid crystals (sodium decyl sulfate, sodium sulfate, decanol, water) have resulted in significant findings. These are: (1) a number of phase transitions occur between 20 and 60°C; (2) these transitions evidence strong critical behavior and long correlation times for fluctuations; (3) and liquid crystals can be studied by light scattering in a unique and meaningful manner. Based on these data it has been concluded that various transitions take place in these lyotropic liquid crystals involving micelle-micelle interactions, hydrocarbon chain reorganizations, and polar head group/counterion/H_2O reorganizations at the micelle surface.

Polymer studies were conducted on ordered polymer systems in both the solid and liquid crystalline solution states. These included PBT - polybenzothiazole and PBO - Polybenzobisoxazole.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Property-Structure-Processing Relations in Polymeric Materials

2. PRINCIPAL INVESTIGATORS:

Dr. Guy C. Berry Chemistry Department Carnegie-Mellon University Pittsburgh, PA 15213	Dr. Hershel Markovitz Chemistry Department Carnegie-Mellon University Pittsburgh, PA 15213

3. INCLUSIVE DATES: 1 August 1977 - 31 July 1981

4. GRANT NUMBER: AFOSR-77-3404

5. COSTS AND FY SOURCE: $36,783, FY77; $37,259, FY78; $54,932, FY79; $54,992, FY80

6. SENIOR RESEARCH PERSONNEL:

Dr. K. Tsutsui
Dr. L. Yen

7. JUNIOR RESEARCH PERSONNEL:

D. B. Cotts
D. W. Meitz

8. PUBLICATIONS:

"Rheology of Some Polymeric Systems," H. Markovitz and G. C. Berry, Prod. Res. Dev., 17(2), 95 (1978).

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"Rheology," H. Markovitz, in "AIP Anniversary Physics Vade Mecum," H. L. Anderson, Editor-in-Chief, Chapter 19, American Institute of Physics, New York, 1981.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Kinetics of Polymerization of Rodlike Macromolecules

In recent years, macromolecules with a rodlike chain conformation have been processed from liquid crystalline solutions to prepare fibers and sheets with exceptional stiffness and strength. In this study, the polymerization kinetics of a rodlike chain have been determined. The chain studied, poly(1, 4 phenylene benzobisoxazole), PBO, is rigid and rodlike, forms liquid crystalline solutions, and can be fabricated to give high modulus fibers. The investigation showed that the effective reactivity of the chain decreased sharply with increasing chain length. Presumably, this reflects a diffusion-limited polymerization rate for the condensation of rigid rodlike chains--the reactive end group is not free to diffuse without corresponding motion of the entire molecule, in distinction to the situation with flexible-chain polymers. One result of the unusual polymerization kinetics is that the molecular weight distribution is unusually narrow for a step-growth polymer owing to the relative decrease in the production of long chains and the depletion of short chains in the overall population.

Suspensions in Polymeric Fluids

The purpose of this part of the investigation was to study the rheological properties of polymeric fluids containing suspended particles. Materials of this type find wide application as sealants, coatings, adhesives, etc.

Under this grant we have chosen to study well-characterized dispersions of spherical particles (crosslinked polystyrene, 0.2 μ in diameter) in a polymer solution (narrow molecular weight distribution polystyrene in dioctyl phthalate).

To characterize the rheological properties requires a number of different experimental techniques. We have studied (a) η_χ the viscosity as a function of rate of shear in steady-state shearing flows and (b) the time-dependent (viscoelastic) behavior as reflected in R_χ the recoverable compliance obtained by measuring the strain recovered after the stress is removed following steady simple shearing at the shear rate χ.

The behavior observed with these dispersions is qualitatively different from that found with polymer melts and solutions--particularly at low rates of shear. As χ decreases, the η_χ appears to increase indefinitely without indicating an actual yield value and R_χ, which is a measure of the elastic character of the fluid, approaches a limiting value which can be many orders of magnitude higher than that of the suspending fluid. The dependence of η_χ and R_χ on the concentration of the suspended particles has been determined.

These steady-state measurements have been augmented by studies of the creep compliance $J_\sigma(t)$ determined with a shear stress σ, the transient recovery $R_\sigma(t)$ following steady-state deformation under a shear stress σ, and the storage and loss compliances $J'(\omega)$ and $J''(\omega)$, respectively, determined at small strain amplitudes. The results show that $J_\sigma(t)$ is equal to $R_0(t)$ (the limiting value of $R_0(t)$ for small σ) so long as the imposed strain $\gamma = \sigma J_\sigma(t)$ is smaller than a value γ_c that is small (ca. 0.01) and decreases with increasing bead content. For $\gamma > \gamma_C$, $J_\sigma(t)$ deviates from equality with $R_0(t)$ and has a fluid-like limiting behavior with $\partial J_\sigma(t)/\partial t = \eta_\chi^{-1}$, where η_χ is the parameter defined above. For $\gamma < \gamma_c$, $J(t)$ is found to be equal to the dynamic compliance $|J^*(\omega)|$ for $\omega = t^{-1}$ (here, $|J^*|^2 = (J')^2 + (J'')^2$); this correspondence, while not rigorous, is frequently observed with diverse materials.

These rheological data thus indicate that the suspensions of beads in a polymeric fluid are solidlike for small imposed strains (e.g., for $\gamma < \gamma_c \sim 0.01$), and fluidlike for strains in excess of a critical value. Electron microscopy on surface replicas prepared from fractured suspensions cooled to the glassy state reveal a substantial order among the beads, which tend to be an hexagonal closepacked array. The rheological data shows that 1) this order is global with irregular aggregates of macroscopic dimensions, even at relatively low bead content, giving the suspensions solidlike behavior in shearing deformation (including a deformation for which the strain amplitude is oscillatory in time) provided the strain is smaller than a critical value, and 2) the bead structure may be partially disrupted to permit 'flow' at large strains with the structure retention dependent on the shear rate.

It is proposed that the bead structure is stabilized by the loss of entropy suffered by macromolecules in the suspending solution as they come near a bead surface. Organization of the beads is consequently stabilized by osmotic effects that arise owing to reduced polymer concentration in regions between closely spaced beads. Consequently, the suspension develops solidlike properties, even without the intervention of specific attractive forces between the beads or any shape asymmetry that might promote an ordered state. It is believed that the principles elucidated by this study should aid in the understanding of those more complex systems.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: The Structure and Properties of Polymeric Materials

2. PRINCIPAL INVESTIGATOR: Dr. P. J. Flory
Department of Chemistry
Stanford University
Stanford, CA 99305

3. INCLUSIVE DATES: 1 February 1977 - 30 September 1981

4. GRANT NUMBER: AFOSR-77-3293

5. COSTS AND FY SOURCE: $83,000, FY77; $65,000, FY78; $71,685, FY79; $33,773, FY80; $68,000, FY81

6. SENIOR RESEARCH PERSONNEL: Dr. J. E. Mark

7. ASSOCIATE RESEARCH PERSONNEL:

D. Y. Yoon
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E. Saiz
B. Erman
W. Wagner
A. Abe
R. S. Frost
H. Pak
G. Ronca
J. P. Hummel
R. R. Matheson

8. PUBLICATIONS:

"Analysis of Nuclear Magnetic Resonance Spectra of Protons in Predominantly Isotactic Polystyrene," D. Y. Yoon and P. J. Flory, Macromolecules, 10, 562 (1977).

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"Moments of the End-to-End Vectors for p-Phenylene Polyamides and Polyesters," B. Erman, P. J. Flory, and J. P. Hummel, *Macromolecules*, *13*, 484 (1980).

"Elastic Modulus and Degree of Cross-Linking of Poly(Ethyl Acrylate) Networks," B. Erman, W. Wagner, and P. J. Flory, *Macromolecules*, *13*, 1554 (1980).

"Statistical Thermodynamics of Mixtures of Semi-Rigid Macromolecules: Chains with Rodlike Sequences at Fixed Locations," R. R. Matheson, Jr. and P. J. Flory, Macromolecules, in press.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to relate the physical and mechanical properties of polymers to their chemical structures. In particular, the statistical mechanical theory of rigid and semi-rigid chains addressed the theory of polydisperse systems of rodlike particles subject to orientation-dependent interactions and of their mixtures with diluents. The prediction of order parameters for nematic phases and the effects of randomly cooled units occurring in the same chain with rigid sequences were investigated. Experiments on phase equilibria in nematogenic systems addressed isotropic-nematic equilibria in oligomers of p-hydroxy-benzoic acid and lyotropic systems. Rubber elasticity research focused on strain-birefringence in poly(ethyl acetate) and polystyrene.

Research has extended theory of the liquid crystalline state in polymers in several directions, particularly the statistical thermodynamics of mixtures of rodlike particles. Polydispersity in polymers has been treated and important implications of the theory of poly-disperse systems have been revealed. Species differing in length are predicted to be selectively partitioned between coexisting nematic and isotropic phases, for example. This prediction has been confirmed by experiments carried out in other laboratories.

The combinatory partition function for a system of rodlike particles of diverse axis ratios mixed with a quasispherical solvent were derived by use of the model and elaboration of the procedure previously employed for a binary system in which the solute is monodisperse. A single disorder parameter $y = x \sin \Psi_x$, where x is the axis ratio for solute particles of a given component and $\sin \Psi_x$ measures their average inclination with respect to the axis of the domain, or phase, characterizes all solute components for which $x > y$. Components with $x < y$ are unoriented. Chemical potentials were given for the various components, and the basic relations required for treatment of the equilibria between an isotropic and an anisotropic, or liquid crystalline, phase derived.

Phase equilibria have been calculated for athermal, three-component systems comprising a solvent with axis ratio $x_1 = 1$ and two solutes consisting of rodlike particles with axis ratios x_a and x_b, respectively, equal to (40,20), (100,20), and (100,10). The small immiscibility gaps separating the isotropic (dilute) from the anisotropic (more concentrated) phase in the respective two-component systems (1,a) and 1,b) were enlarged by addition of the second solute component. The species a and b, with $x_a > x_b$, occur preferentially in the anisotropic and isotropic phases, respectively. The component with axis ratio $x_a = 100$ is virtually excluded from the isotropic phase when the amount of the smaller component ($x_b = 10$ or 20) in the system is more than a few percent of a. Triphasic equilibria were predicted for the systems x_a, x_b = 100,20 and 100,10.

Biphasic equilibria were investigated for athermal mixtures in which the solute comprises rodlike particles having the familiar distribution $v_x^0 = v_2^0(1 - p)^2 xp^{x-1}$, x being both the number of units and the axis ratio. Under conditions such that the volumes of the coexisting phases are comparable, the polydispersity in each phase is considerably lower than for the parent ("most probable") distribution. Fractionation between the phases is remarkably efficient. A concomitant of the preferential partioning of lower and higher species between the respective phases is the broad range of overall concentration within which the system is biphasic. The undiluted polydisperse solute is predicted to be biphasic for $(1 - p)^{-1}$ in the range ~ 2.3-17.5. It is isotropic below this range and wholly anisotropic for greater average chain lengths $\bar{x}_n^0$. According to theory, an isotropic phase in which the solute retains the foregoing distribution can coexist in equilibrium with an anisotropic (nematic) phase only if this phase comprises species of very large x at high concentration in ordered array. This deduction follows regardless of the average $\bar{x}_n^0 = (1 - p)^{-1}$ in the isotropic phase provided only that $\bar{x}_n^0 > 2.3$. If interchange processes $M_{x1} + M_{x2} \rightleftarrows M_{x1+x2}$ occur freely at random, continuous transformation to a highly ordered anisotropic phase is predicted. Thus, formation of rodlike particles through random, linear aggregation of subunits offers an exceptionally simple scheme for self-ordering.

Biphasic equilibria in systems comprising rodlike solute particles having a Poisson distribution of lengths, these being in admixture with a solvent, were treated by adaptation of theoreticl relationships presented in the preceding papers. Selective partitioning of solute species between coexisting isotropic and anisotropic phases occurs, but its effect diminishes as the average length $\bar{x}_n^0$ (or axis ratio) of the rodlike particles increases and the polydispersity of the Poisson distribution simultaneously decreases. The biphasic gap is much narrower than for the most probable distribution. When x_n^0 is large, concentrations of the coexisting phases and other characteristics of the heterogeneous system formed from a Poisson distribution of solute species conform closely to those for the binary mixture of solvent and monodisperse rods with axis ratio $x = \bar{x}_n^0$.

Ternary systems consisting of a solvent (1), a rigid rod solute (2), and a randomly coiled polymer chain (3) were treated according to the model and procedures employed in part 1. Phase equilibria were calculated for systems specified by $(x_2, x_3) = (10,10), (20,20), (20,\infty)$, and (100,100), where x_2 and x_3 are the molar volumes of the respective solutes relative to the solvent. Addition of component 3 to the binary system 1,2 increases the volume fraction $_2'$ of the rodlike solute in the anisotropic phase and broadens the biphasic gap. The preponderance of component 3 is retained by the isotropic phase. Its volume fraction v_3' in the anisotropic phase is $< 10^{-4}$ for all compositions and becomes vanishingly small if v_2' is much increased by raising v_3 in the isotropic phase. The isotropic phase exhibits a somewhat greater tolerance for the rodlike component (2). For large values of x_2 and v_3, however, v_2 becomes negligible. The marked segregation of these components between the two phases underscores the basic differences in their mixing tendencies. This work has played a leading role inthe Air Force Ordered Polymer Research Program.

Solutions were treated in which the solute molecule comprises m rodlike sequences, each of axis ratio x , connected in linear succession by m -1 joints permitting free orientations. Separation of an anisotropic phase depends predominantly on x . Increasing the chain length from x to $x_m = mx$ by joining m rods affects the compositions of the phases coexisting at equilibrium by only a few percent. The implications of these results on the behavior to be expected in systems of semirigid real chains of various types were determined.

The part played by orientation-dependent interactions between nematogenic molecules was incorporated in the theory. Although secondary to particle shape in importance, such interactions contribute significantly to the stability of liquid crystalline phases formed from low molecular nematogens. They are doubtless important also in polymers prone to yield liquid crystalline domains, especially those containing aromatic groups within their chains.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Chemical and Physical Aspects of Mesophase Formation during Carbon-Carbon Processing

2. PRINCIPAL INVESTIGATOR: Dr. J. J. Gebhardt
Re-entry Systems Division
General Electric Company
Philadelphia, PA 19101

3. INCLUSIVE DATES: 1 December 1977 - 31 January 1981

4. CONTRACT NUMBER: F49620-78-C-0006

5. COSTS AND FY SOURCE: $50,300, FY78; $63,306, FY79; $53,735, FY80; $20,963, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. J. O. Hanson
J. A. Roetling
F. G. Rouse

7. PUBLICATIONS:

"Chemical and Physical Aspects of Mesophase Formation during Carbon-Carbon Processing,' J. J. Gebhardt, Final Technical Report, F49620-78-C-0006, Jan 1981.

"Thermal Conductivity of Coal Tar Pitch by Flash Diffusivity," J. O. Hanson and J. J. Gebhardt, Carbon, 19, 141, 1981.

"Viscosity of Some Polyaromatic Hydrocarbons to 101 MPa," J. J. Gebhardt, J. A. Roetling, and F. G. Rouse, Proceedings, 15th Biennial Conference on Carbon, p 172, June 1981.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The advent of carbon-carbon composites has brought about a need for more rapid, precise and controlled graphite formation from liquid precursors within the voids and interstices of arrays of preassembled fiber bundles than has heretofore been required. Simultaneously, variations in pitch raw stocks, not unusual for an industrial 'natural' product, have made it more difficult to predict composite fabrication and performance on the basis of the properties of 'typical' available raw materials. A further requirement for shortened production schedules has led to impregnation and coking of the pitch within the preforms at elevated pressures while at the same time expanded use of carbon-carbon composites has increased not only the volume to be processed, i.e., densified, but also preform sizes and geometries.

As a consequence there has arisen a need to know more precisely some of the physical and chemical responses of polynuclear molecules and mixtures, such as coal tar pitch at elevated pressures and temperatures. This is particularly so of transport property data such as viscosity and thermal diffusivity and conductivity needed to permit prediction of processing parameters and rates of change to be used in impregnation and pyrolysis within relatively fragile and expensive preforms. Rates of heating, pressure application, impregnation and penetration, gas formation and percolation, liquid exudation and finally coke yield and distribution within the preform can be expected to be influenced by changes in pitch properties with time at temperature and pressure. Preform strength and integrity can also be compromised by unexpected internal stress buildup due to imbalances in the pressure-temperature response of the impregnated, reacting pitch.

The purpose of this research was to generate an understanding of the nature and composition of coal tar and petroleum pitch with respect to mesophase and graphite formation at atmospheric as well as elevated pressure. This was accomplished by direct determination of selected transport properties of an accepted coal tar pitch standard as well as observations of its behavior during the early phases of mesophase formation under pressure.

Experimental studies were carried out to elucidate some of the effects of pressure on properties of coal tar pitch materials and simpler fused ring compounds. Sound velocity measurements were made on phenanthrene up to 562K and 101 MPa and on Allied 277-15V pitch up to 541K at 0.1 MPa. The latter deviated markedly from the nearly linear relationship between sound velocity and temperature found for phenanthrene. Adiabatic compressibilities at 0.1 MPa were calculated.

A high pressure falling needle viscometer was constructed and calibrated. Relative viscosities of naphthalene, phenanthrene and Allied 277-15V pitch were measured at pressures up to 101 MPa and at temperatures up to 373, 573 and 608K respectively. Naphthalene and phenanthrene showed a twofold increase between 0.1 and 101 MPa, while a sixfold increase was measured for the pitch specimen.

A melting point-pressure curve was established for naphthalene based on observed temperature variations during pressure changes. The pitch specimen gave qualitative evidence of partial solidification around 50 MPa and 533K.

Thermal diffusivity and conductivity were measured on as-received and partially pyrolyzed specimens of 277-15V pitch and two developmental Koppers Co. pitches, using a laser flash technique. Minor trends to lower conductivity were noted for short pyrolysis times; the conductivity then rose slightly on further pyrolysis.

Pyrolysis analytical results and optical and scanning microscopy observations showed a positive effect of pressure on rate of conversion and noticeable repression of turbulence and percolation of 6.2 MPa. All three pitch materials appear to contain or to form an immiscible phase during pyrolysis, which collects inside gas bubbles and cracks in the unconverted regions of the specimen.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Laser Hole Burning Spectroscopy: A High Resolution Probe of Molecular Environments

2. PRINCIPAL INVESTIGATOR: Dr. R. M. Macfarlane
IBM Research Laboratory
San Jose, CA 95193

3. INCLUSIVE DATES: 1 June 1979 - 31 May 1981

4. CONTRACT NUMBER: F49620-79-C-0108

5. COSTS AND FY SOURCE: \$19,600, FY79; \$59,189, FY80; \$40,932, FY81

6. SENIOR RESEARCH PERSONNEL: Dr. R. M. Shelby

7. COLLABORATIVE RESEARCH PERSONNEL:

Dr. G. C. Bjorklund
Dr. D. P. Burum
Dr. M. D. Levenson
Dr. W. Lenth
Dr. C. Ortiz
Dr. C. S. Yannoni

Dr. R. L. Shoemaker, University of Arizona, Tucson, Arizona
Dr. A. Z. Genack, Exxon Research, Linden, New Jersey
Dr. D. A. Weitz, Exxon Research, Linden, New Jersey
Professor A. Schenzle, University of Essen, West Germany

8. PUBLICATIONS:

"Laser Hole Burning Spectroscopy: A High Resolution Probe of Molecular Environments," R. M. Macfarlane and R. M. Shelby, Final Technical Report, 1981.

"Ultra-High Resolution Spectroscopy: Photon Echoes in $YAlO_3:Pr^{3+}$ and $LaF_3:Pr^{3+}$," R. M. Macfarlane, R. M. Shelby, and R. L. Shoemaker, Phys. Rev. Lett., 43, 1726 (1979)

"Optical Line Narrowing by Nuclear-Spin Decoupling in $Pr^{3+}:LaF_3$," R. M. Macfarlane, C. S. Yannoni, and R. M. Shelby, Opt. Comm., 32, 101 (1980).

"Optical Measurement of Spin-Lattice Relaxation in Dilute Nuclei - $Pr^{3+}:LaF_3$," R. M. Shelby, R. M. Macfarlane, and C. S. Yannoni, Phys. Rev., B21, 5004 (1980).

"Laser Hole Burning Spectroscopy of Solids," R. M. Macfarlane and R. M. Shelby, J. Opt. Soc. Am., 70, 583 (1980).

"Observation of Very Narrow Optical Resonances in Solids Using Photon Echoes," R. M. Shelby and R. M. Macfarlane, J. Opt. Soc. Am., 70, 613 (1980).

"Coherent Transients by Optical Phase Switching: Dephasing in Pr^{3+}:$LaCl_3$, A. Z. Genack, D. A. Weitz, R. M. Macfarlane, R. M. Shelby, and A. Schenzle, Phys. Rev. Letters, 45, 438 (1980).

"Polarization Spectroscopy Measurement of the Homogeneous Linewidth of an Inhomogeneously Broadened Color Center Band," M. D. Levenson, R. M. Macfarlane, and R. M. Shelby, Phys. Rev., B22, 4915 (1980).

"Measurement of Nuclear and Electronic Zeeman Effects Using Optical Hole Burning Spectroscopy," R. M. Macfarlane and R. M. Shelby, Opt. Lett., 6, 96 (1980).

"Frequency Dependent Optical Dephasing in the Stoichiometric Material EuP_5O_{14}," R. M. Shelby and R. M. Macfarlane, Phys. Rev. Letters, 45, 1098 (1980).

"Nuclear Quadrupole Optical Hole Burning in the Stoichiometric Material EuP_5O_{14}," R. M. Macfarlane, R. M. Shelby, A. Z. Genack, and D. A. Weitz, Opt. Lett., 5, 462 (1980).

"Thin-Film Aggregate Color Centers as Media for Frequency Domain Optical Storage," C. Ortiz, R. M. Macfarlane, R. M. Shelby, W. Lenth, and G. C. Bjorklund, Appl. Phys., 25, 87 (1981).

"Sub-kilohertz Optical Linewidths of the $^7F_0 \leftrightarrow {}^5D_0$ Transition in Y_2O_3:Eu^{3+}, R. M. Macfarlane and R. M. Shelby, Opt. Comm. (to be published).

"Optical Hole Burning by Superhyperfine Interactions in CaF_2:Pr^{3+}," R. M. Macfarlane, R. M. Shelby, and D. P. Burum, Opt. Lett. (to be published).

"Measurement of the Anomalous Nuclear Magnetic Moment of Trivalent Europium," R. M. Shelby and R. M. Macfarlane, Phys. Rev. Lett., October 19, 1981.

"Hole Burning ODNMR in Pr^{3+}:CaF_2." D. P. Burum, R. M. Shelby and R. M. Macfarlane, Phys. Rev. B (submitted).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Spectral hole burning is a process whereby a narrow "hole" is bleached in an inhomogeneously broadened line following irradiation by a narrow band laser. This is caused by the removal of a subset of ions or molecules from their ground state to a level where they no longer absorb the laser light. In cases where there is a fine structure in the electronic excited state (e.g., due to hyperfine interactions, external fields, etc.) this structure shows up as subsidiary side holes. The width of these holes, their dynamics and their behavior under applied perturbations gives valuable spectroscopic information relating to the environments of the active species. In addition, the phenomenon of hole burning provides the basis for frequency domain optical information storage. Laser induced hole burning in optical absorption bands of low temperature solids has been investigated with emphasis on mechanisms for population hole burning, the interactions with the environment which limit the hole widths and the use of hole burning for ultra high resolution spectroscopy.

Hole burning was observed in a wide range of solids including organic and organometallic molecules in crystals and rare earth ions in crystals and glasses. The mechanisms for hole burning also varied widely and a new mechanism involving optically induced nuclear spin flips of near neighbor nuclei was discovered. Examples of hole burning in new classes of materials were presented for the first time, namely inorganic glasses (silicate glasses containing Nd^{3+}, Pr^{3+} or Eu^{3+}) and undoped stoichiometric compounds (e.g., EuP_5O_{14}). Hole recovery was used to determine nuclear spin lattice relaxation rates in praseodymium doped crystals. For allowed optical transitions (e.g., singlet states of zinc porphyrin, dibromoindigo and color centers in alkali halides) the hole widths at 2K are limited by population decay to approximately 50 MHz. For longer lived optical levels in crystalline materials, e.g., those containing rare earth ions, the hole widths are narrower (less than 10 MHz) and are limited by dynamical interactions with surrounding nuclei. In amorphous materials such as europium doped silicate glass, hole widths are much broader, being limited by low frequency tunneling motions. Hole burning measurements were complemented by time domain coherent transient (photon echo and optical free decay) measurements of homogeneous linewidths which enabled us to measure optical resonances as narrow as 760 Hz in $Eu^{3+}:Y_2O_3$. In cases where hold burning involved optical pumping of nuclear hyperfine levels, optically detected nuclear resonance was used to investigate the dynamics of nuclear spins which were responsible for hole broadening and optical dephasing.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Solid State Reactions in Polymeric Materials.

2. PRINCIPAL INVESTIGATOR: Dr. Paras N. Prasad
Department of Chemistry
State University of New York
Buffalo, New York 14214

3. INCLUSIVE DATES: 1 September 1978 - 31 August 1981

4. GRANT NUMBER: AFOSR-78-3676; F49620-79-C-0229;
AFOSR-80-0287

5. COSTS AND FY SOURCE: $39,225,FY78; $63,859,FY79; $58,388,FY80

6. SENIOR RESEARCH PERSONNEL:

Dr. K. Dwarakanath
Dr. J. Swiatkiewicz

7. JUNIOR RESEARCH PERSONNEL:

L. A. Hess
B. A. Bolton
G. Eisenhardt
R. R. McCaffrey
F. Szlazda

8. PUBLICATIONS:

"Vibrational Relaxation in a Structurally Disordered Solid: Temperature Dependence of Raman Active Phonons in p-Bromochlorobenzene and p-Dichlorobenzene," P. N. Prasad, and R. V. Smith, J. Chem. Phys. 71, 4646 (1979).

"Vibrational Dephasing in Organic Solids: Temperature Dependence of a Localized Raman Active Internal Mode of Naphthalene," L. A. Hess and P. N. Prasad, J. Chem. Phys. 72, 573 (1980).

"Vibrational Relaxations and Dephasing in Organic Solids," P. N. Prasad, Mol. Cryst. Liq. Cryst. 58, 39 (1980).

"Raman Phonon Spectroscopy of Solid State Reactions: Thermal Rearrangement of Methyl-p-Dimethylaminobenzene Sulfonate in Solid State," K. Dwarakanath and P. N. Prasad, J. Am. Chem. Soc. 102, 4254 (1980).

"Laser Raman Spectroscopic Investigation of Pharmaceutical Solids, Griseofulvin and its Solvates", B. A. Bolton and P. N. Prasad, J. Pharm. Sci. 70, 789 (1981).

"Structure and Dynamics of the Iodine Column in the Polyiodine Canal Complexes $(\text{Benzophenone})_9 (KI)_2 I_7 CHCl_3$" B. A. Bolton and P. N. Prasad, Mol. Cryst. Liq. Cryst. 76, 309 (1981).

"Phonon Spectroscopy of Photochemical Reactions in Organic Solids", J. Swiatkiewicz, G. Eisenhardt, P. N. Prasad, W. Jones, J. M. Thomas, and C. R. Theocharis J. Phys. Chem. (in Press).

"Dephasing of Optical Phonons in a Substitutionally Disordered Organic Solid: The Lowest Frequency Raman Active Phonon of a Binary Solid Solution between p-Bromochlorobenzene and p-Dichlorobenzene", L. A. Hess and P. N. Prasad, submitted to J. Phys. Chem.

"Low Frequency Raman Spectroscopic Investigation of Polymer Blends", G. Eisenhardt, B. A. Bolton and P. N. Prasad, manuscript under preparation.

"Phonon Spectroscopy of Dynamics of Solid State Polymerization Process", J. Swiatkiewicz and P. N. Prasad, manuscript under preparation.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objectives of this research was to formulate an understanding, at the molecular level, of the reactivity and function of monomeric and polymeric materials in a condensed phase. A novel approach utilizing phonon spectroscopy was successfully used for this study. Two specific aims for developing a dynamic model of reactivity in the solid state were: (i) Application of Raman phonon spectra to determine if a reaction in solid proceeds by a homogeneous mechanism (the reactant and the product form a solid solution) or by a heterogeneous mechanism (the reactant and the product form two separate phases). (ii) Understanding the role of phonon motions in influencing the reactivity in a condensed phase. Significant accomplishments are achieved on both points. By monitoring Raman phonon spectra as a function of the reaction progress the following solid state reactions were found to be heterogeneous: (i) Photodimerization of α- and β-transcinnamic acids; (ii) Thermal rearrangements of methyl-p-dimethylaminobenzene sulfonate which yields p-trimethylammonium benzene sulfonate zwitterion; and (iii) photopolymerization of 2,5-distyrylpyrazine in the α-phase. On the other hand, the following reactions were found to be homogeneous; (i) Photodimerization of 2-benzyl-5-benzylidene cyclopentanone; and (ii) thermal polymerization of diacetylenes, specifically bis-(p-toluene sulfonate) ester of 2,4-hexadiyene-1,6-dial.

The approach of phonon spectroscopy also led us to propose a new concept of phonon-assisted reactions. In the case of the thermal rearrangement of methyl-p-dimethylaminobenzene sulfonate, softening of a 30 cm^{-1} phonon mode was observed as a function of temperature. It was proposed that the softening of this specific mode leads to large amplitude oscillations in the lattice. The reaction is assisted by these large amplitude oscillations. The phonon spectroscopic studies using electronic spectroscopy provide support for our novel concept of phonon-assisted photochemical reactions. The low temperature (4°K) electronic spectra of both 2-benzyl-5-benzylidene-cyclopentanone and 2,5-distyrylpyrazine crystals show strong electron-phonon coupling in the reactive excited electronic state. It was proposed that the strong electron-phonon coupling in the reactive excited electronic state leads to trapping of the energy. It also leads to local performation of the product lattice. These two effects assist the reaction.

Other related areas where research was accomplished are: (a) Vibrational relaxation in organic solids. This study was necessitated from a need to formulate conditions under which a selective vibrational as well as phonon excitation could be used to produce novel products by state selected chemistry. Using temperature dependence of Raman spectra we found that the lowest frequency optical phonons in p-bromochlorobenzene, p-dichlorobenzene decay by a T_1-mechanism involving cubic anharmonic interactions. On the other hand, for the 764 cm^{-1} intramolecular mode of naphthalene a T_2' process involving a quartic anharmonic interaction was found to be dominant. (b) Raman phonon study of pharmaceutical solids in relation to their bioavailability. The method of Raman phonon spectroscopy was introduced as a convenient technique to study various solid state forms of a given drug and their physical and chemical stabilities. Specifically, the drug griseofulvin was studied. (c) Structure and dynamics of the conducting complex: $(\mathrm{Benzophenone})_9\,(\mathrm{KI})_2\,\mathrm{I_7CHCl_3}$. By the resonance Raman method this complex was found to contain $\mathrm{I_3^-}$ and the $\mathrm{I_3^-/I_2}$ complex in a random dynamic equilibrium. It was found that the substitution of the solvent ($\mathrm{CHCl_3}$) had only small effect on the iodine interaction. However, changing the cation from $\mathrm{K^+}$ to Li produces a more ordered structure with regular (but bent) $\mathrm{I_5^-}$ species. (d) Phonon spectroscopy of polymeric alloys. This new method was introduced to determine the molecular homogeneties of polymer blends. With this method, a polymer blend of polystyrene and 2,6-dimethylpolyphenylene oxide was found to be a homogeneous alloy at the molecular level.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Microstructure of Amorphous and Semi-Crystalline Polymers

2. PRINCIPAL INVESTIGATOR: Dr. D. R. Uhlmann
Department of Materials Science
and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

3. INCLUSIVE DATES: 1 February 1977 - 31 October 1980

4. GRANT NUMBER: AFOSR-77-3226

5. COSTS AND FY SOURCE: $43,000, FY77; $45,000, FY78; $48,500, FY79; $38,000, FY80

6. SENIOR RESEARCH PERSONNEL: Dr. J. Vander Sande

7. JUNIOR RESEARCH PERSONNEL:

M. Meyer
M. Matyi
G. Di Filippo
B. Jang

8. PUBLICATIONS:

"Microstructure of Amorphous and Semi-Crystalline Polymers," D. R. Uhlmann, Final Technical Report, AFOSR-77-3226, June 1981.

"Electron Microscopy and SAXS Studies of Amorphous Polymers," D. R. Uhlmann, Faraday Discussions of the Royal Society of Chemistry, 68, 22 (1979).

"Polymer Glasses and Oxide Glass," D. R. Uhlmann, Journal of Non-Crystalline Solids, 42, 119 (1980).

"On the Structure of Glassy Polymers. VI. Electron Microscopy of Polycarbonate, Poly(ethylene Terephthalate), Poly(vinyl Chloride), and Polystyrene," M. Meyer, J. Vander Sande, and Dr. R. Uhlmann, Journal of Polymer Science: Polymer Physics Division, 16, 2005 (1978).

"Structure of Glassy Polymers. VII. Small-Angle X-Ray Scattering from Epoxy Resins," R. J. Matyi and D. R. Uhlmann, Journal of Polymer Science: Polymer Physics Division, 18, 1053 (1980).

"On the Structure of Glassy Polymers, VIII. Electron Microscopy of Stained Thermoplastics," G. V. Di Filippo, J. B. Vander Sande and D. R. Uhlmann, Journal of Polymer Science: Polymer Physics Division (submitted for publication)

"On the Structure of Glassy Polymers. IX. Z Contrast Electron Microscopy," G. V. Di Filippo, J. B. Vander Sande, and D. R. Uhlmann, Journal of Polymer Science: Polymer Physics Division (submitted for publication).

"The Atomic Structure of Glasses," D. R. Uhlmann, Amorphe Festkorper, 2. Tagung Festkorper Physik, p. 64, 26-28 Nov 1980, Physikalische Gesellschaft der Deutschen Demokratischen Republic, Rostock.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This present research program focused on identification of the important microstructural features of amorphous and semi-crystalline polymers, and the relation of these features to processing and to the mechanical, optical and electrical properties of the materials. The study of amorphous polymers centered on thermosetting resins, with particular attention directed to epoxy, polyimide and phenolic resins. Semi-crystalline polymers were studied with attention on the chemical and structural differences between bulk material and near-surface regions, on structural features produced by crystallization under high thermal gradients, and on differentiating between adjacent re-entry folding and switchboard models for the basic structural units in semi-crystalline polymers. This work employed a range of crystallization conditions, including quiescent and flowing melts, large and small thermal gradients and high pressures, and a wide range of analytical techniques. In all cases, the microstructural variations were related to measurements of mechanical, optical, and electrical properties.

Work carried out under this grant has led to the development of a technique for scanning transmission electron microscope of polymers which seems to offer outstanding promise for the characterization of their structures. When applied to amorphous thermoplastics, the structures are found to be homogeneous down to the limit of resolution to the microscope, with no evidence found for the presence of nodular features or other structures characteristic of regions of local order in the materials. This finding is in accord with the results of small angle X-ray scattering studies of the same materials. Based on the combined results of these studies, it is suggested that the nodular hypothesis be laid to rest and that the structure of flexible chain amorphous polymers be represented by models such as the random coil. The technique of microtoming bulk samples followed by staining with heavy metal atoms and viewing with Z contrast in the scanning transmission electron microscope has also been used with success to characterize the structures of epoxy and polyimide resins. Commercial polyimide films have been shown to be homogeneous on a scale of 50-200 A, with the scale and form of the heterogeneities varying through the thickness of the film. The structure of epoxy resins presents a more complicated issue. For some resins and some curing conditions, heterogeneous microstructures can be observed. In these cases, the typical scale of the heterogeneities is in the range of 100-200 A.

For other epoxy resins and other curing conditions, however, substantially homogeneous microstructures are produced. It seems, therefore, that the production of heterogeneous structures is not a characteristic feature of thermosetting resins. It also seems clear that the structure of the cured resins, as well as their properties and performance characteristics, will depend in detail on the resin and conditions of cure. In conclusion, it appears that the technique of high resolution, high contrast electron microscopy--carried out with the scanning transmission electron microscope--is veritably in its infancy. The technique seems to offer particular promise for characterizing the structure of polymers since it permits high contrast images to be obtained with a minimum of electron irradiation and with a permanence to the structural features. It is anticipated that this technique will find many applications during the coming decade.

AFOSR Program Manager: Dr. Donald R. Ulrich

COMPLETED PROJECT SUMMARY

1. TITLE: Stabilization of Acrylic Fibers and Microstructure of Carbon-Carbon Composites

2. PRINCIPAL INVESTIGATOR: Dr. D. R. Uhlmann
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA 02139

3. INCLUSIVE DATES: 20 September 1977 - 19 September 1980

4. GRANT NUMBER: AFOSR-77-3466

5. COSTS AND FY SOURCE: $46,530, FY77; $47,000, FY78; $51,577, FY80

6. SENIOR RESEARCH PERSONNEL: Dr. L. H. Peebles

7. JUNIOR RESEARCH PERSONNEL:

I. G. Plotzker
J. H. Cranmer
C. B. Brogna

8. PUBLICATIONS:

"Stabilization of Acrylic Fibers and Microstructure of Carbon-Carbon Composites," D. R. Uhlmann, Final Technical Report, AFOSR-77-3466, June 1981.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to systematically study how process variables influence the chemical reactions and structural changes which take place in the conversion of acrylic fibers to carbon fibers and the influence of the fibers on the composite matrix mesophase precursor. This research contributed to the establishment of the process science base essential to meeting the requirements of propulsion and reentry grade carbon fibers and composites. Research focused on a systematic study of - 1) the effects of changes in the stabilization conditions on the texture of stabilized acrylic fibers, as well as a determination of the influence of the stabilization conditions on the microstructure and properties of the final carbon fibers, and 2) the development of microstructure during the processing of carbon-carbon composites, and the relation between structural features of the composites and the structure of the carbon fibers.

The investigation of the stabilization of acrylic fibers and the development of structure in fabricating carbon-carbon composites has directed attention to the structural features of the materials, their variation with processing and their implications for the properties of the final materials. The work on the stabilization of acrylic fibers has demonstrated that various mantle-core structures are observed at intermediate stages of stabilization, that the dark mantles seen in optical thin sections can be related to the etched mantles seen on exposure to solvents for polyacridonitrile (PAN), that the mantles seen on fractured fiber ends reflect the underlying structure of the partly-stabilized fibers, that the development of these various mantles with time depends on the nature of the precursor fibers and the processing conditions, that liquid droplets can be produced during fracture of fibers during stabilization, and that the fracture of even a small number of fibers can produce effective cementation of a yarn during processing. The study of the interaction between mesophase material and carbon fibers has directed attention to the precipitation, growth and coalescence of mesophase material, which processes require ordering of small molecules in a viscous medium. On this basis, dynamic motion in the fluid rather than the presence of nucleating substrates is suggested to be the controlling factor in the structural development. Where dynamic motion is restricted, as in the interstices of a yarn, mesophase formation and growth are also restricted. Alignment of mesophase material with a substrate is primarily controlled through motion of the mesophase droplets in flow, which generally do not wet the substrate. Certain well-ordered surfaces are wetted by the mesophase material, but the effect is primarily noted on surfaces of comparable size to the droplets.

AFOSR Program Manager: Dr. Donald R. Ulrich

AFOSR SPONSORED RESEARCH IN MOLECULAR DYNAMICS

Major William G. Thorpe

The AFOSR program in molecular dynamics is principally concerned with understanding fundamental processes of energy transfer in gas phase reactions. Anticipated Air Force technology needs in chemical lasers and upper atmosphere modeling are important driving forces. This program is composed of four subareas: chemical lasers, upper atmosphere chemistry, plume and wake chemistry, and interactive dynamics. In 1982, the plume and wake chemistry subarea will be dropped as a separate area because of its small size. A focused program in decomposition kinetics is planned.

New chemical laser candidates are likely to be those in which the chemical pumping species is distinct from the lasing species. In particular, a chemically excited product will collisionally transfer its energy to an atomic or diatomic species which subsequently radiates in the visible or ultraviolet. Consequently, this program will continue to develop a basic understanding of energy transfer dynamics. Current interests are in the development of chemical pumping techniques for iodine monofluoride and the alkali or alkaline earth elements. In addition, the excited states of halogens and interhalogens need to be better spectroscopically characterized.

The atmospheric chemistry subarea is primarily concerned with optical and chemical processes occurring in the upper atmosphere. Current interests include ion-molecule reactions, the understanding of atmospheric reactions involving O, N, O_2, and N_2, and the characterization of aqueous cluster species. These interests incorporate the fundamental research supported in the plume subarea.

A new subarea concerning decomposition kinetics is under consideration. Its objective is the understanding of explosive decomposition mechanisms important in modeling conventional explosives and in understanding aging and thermal degradation processes. Present research in high energy conventional explosives appears to be mainly guided by hydrodynamic issues. It would seem prudent to encourage a more balanced approach. Certainly, the storability issues are directly linked to the chemistry and dynamics of thermal energy dissipation. At the Frank J. Seiler Research Laboratory, preliminary approaches utilizing ESR have been successful in detecting the formation of the dinitrotolyl radical in the thermal decomposition of TNT. Within the context of our program, the emphasis will be on applying optical techniques to elucidate the reaction mechanism. Admittedly, the first results may be less than definitive; nevertheless, it is time to take full advantage of the techniques available to the chemical physics community in this area.

The goal of the approaches in the interactive dynamics subarea concerns a basic understanding of the interaction of optical radiation with chemical species. It encompasses some of the most long range research and enhances the more directed efforts. Supported efforts in this area include inter- and intra-molecular energy transfer processes and the effects of reactant orientation and energy on product formation at a state-to-state level. The capability to effect selected product formation as a function of transition state excitation will be emphasized.

The AFOSR Molecular Dynamics contractors meeting was held in November at the Air Force Weapons Laboratory, Albuquerque, NM. The information exchange between researchers was very productive and a tandem basic research issues discussion concerning HF was extremely productive. The next meeting is planned for 1-3 December 1982 at the USAF Academy, CO. Several investigators supported by the surface chemistry task will be invited to speak.

COMPLETED PROJECT SUMMARY

1. TITLE: Photoionization of Molecular Clusters

2. PRINCIPAL INVESTIGATORS: Dr. R. P. Andres
Dr. J. M. Calo
Department of Chemical Engineering
Princeton University
Princeton, NJ 08544

3. INCLUSIVE DATES: 1 May 1978 - 30 September 1981

4. GRANT NUMBER: AFOSR-78-3638

5. COSTS AND FY SOURCE: $71,928, FY78; $55,711, FY79; $52,808, FY80

6. SENIOR RESEARCH PERSONNEL: G. F. Ryan

7. JUNIOR RESEARCH PERSONNEL: J. J. Kolstad

8. PUBLICATIONS:

"Free Jet Deceleration - A Scheme for Separating Gas Species of Disparate Mass," N. K. Thuan and R. P. Andres, in Rarefied Gas Dynamics, Eleventh Symposium, Vol. 1 (Campargue, Ed.), 667 Commissariat al'Energie Atomique (1979).

"van der Waals Molecules - Possible Roles in the Atmosphere," J. M. Calo and R. S. Narcisi, Geophys. Res. Lett., 7, 289 (1980).

"Fokker - Planck Description of the Free Jet Deceleration Flow," T. K. Nguyen and R. P. Andres, in Rarefied Gas Dynamics, Progress in Astronautics and Aeronautics, 74: Part 1 (Fisher, Ed), 627 (1981).

"Generation of Molecular Clusters of Controlled Size," R. S. Bowles, J. J. Kolstad, J. M. Calo, and R. P. Andres, Surface Science, 106, 117 (1981).

"Melting Temperature of Small Particles," J. Ross and R. P. Andres, Surface Science, 106, 11 (1981).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Hydrated hydronium ions and other water-associated cluster ions dominate the ion chemistry of the lower D region. However, the formation and destruction mechanisms of these species and their chemical and physical properties are not well understood. The theoretical prediction that molecular clusters have lower photoionization thresholds than their constituent molecules and that this threshold decreases with cluster size points to a potential atmospheric source of these ions. Experimental proof of this phenomenon would serve to elucidate, complement, and extend existing theories of atmospheric chemistry, nucleation, and gas-to-particle conversion.

The objective of the research program has been to construct and develop an apparatus for measuring:

A. Photoionization appearance potentials and photoionization cross sections of small molecular clusters known or suspected to be of atmospheric importance.

B. Rate constants for the growth kinetics of both homomolecular water clusters and heteromolecular clusters containing water and other molecules present in the atmosphere.

C. Equilibrium mole fractions of homo- and heteromolecular dimers of atmospheric importance.

An experimental apparatus consisting of a novel multiple expansion cluster source coupled with a molecular beam system and photoionization mass spectrometer has been designed and constructed. This apparatus has been thoroughly tested and preliminary measurements of the growth kinetics of homomolecular water clusters and the photoionization cross section of the water dimer have been carried out.

AFOSR Program Manager: William G. Thorpe, Major, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Diagnostics and Chemical Applications of Multiphoton Absorption Processes

2. PRINCIPAL INVESTIGATOR: Dr. Sidney W. Benson
Department of Chemistry
University of Southern California
Los Angeles, CA 90007

3. INCLUSIVE DATES: 1 April 1977 - 30 September 1981

4. GRANT NUMBER: AFOSR-77-3279

5. COSTS AND FY SOURCE: \$75,000, FY77; \$70,123, FY78; \$68,080, FY79; \$38,450, FY80; \$68,479, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. A. J. Colussi
Dr. J. C. Diels
Dr. P. J. Evans
Dr. P. Papagiannakopoulos
Professor Choi (Korea)

7. JUNIOR RESEARCH PERSONNEL:

Mr. Ken Kosnik

8. PUBLICATIONS:

"Molecular Beam Sampling," A. J. Colussi and Sidney W. Benson, Int. J. Chem. Kin., 10, 1091 (1978).

"Intramolecular Isotope Effects in Laser Multiphoton Dissociation of CH DCH Cl, A. J. Colussi, R. J. Hwang, J. Tiee and Sidney W. Benson, Chem. Phys. Letters, 52, 349 (1977).

"The Prediction of Thermochemical and Kinetic Data for Gas Phase Reactions." (Plenary Lecture). 45h Int. Symp. on Plasma Chemistry, S. W. Benson, Pure and Applied Chem., 52, 1767 (1980).

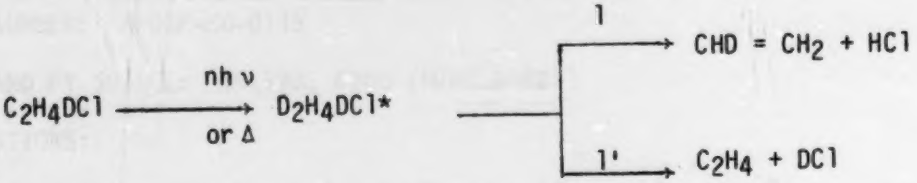
"Intramolecular Isotopic Effect in the Pyrolysis of Ethyl-2d$_1$ Chloride, P. J. Papagiannakopoulos and Sidney W. Benson, Int. J. Chem. Kin. (1982).

"The Effects of Buffer Gases in the Infrared Multiphoton Dissociation of C_2H_4DCl. A Chemical Clock to Explore Highly Excited Molecules," P. J. Papagiannakopoulos, Ken Kosnik, and Sidney W. Benson, Int. J. Chem. Kin. (1982).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

It was the original objective of the present program to develop a simple molecular beam system for examining the effect of various laser parameters on the rate of energy absorption by irradiated molecules. In the course of developing this system the utility of using isotopic branching to accomplish a similar purpose was discovered and to that end the multiphoton dissociation of 2-deuterioethyl chloride, CH_2DCH_2Cl (C_2H_4DCl) was studied.

Excitation of C_2H_4DCl above the activation threshold of about 56 kcal leads to production of HCl or DCl in a concerted molecular process:



A careful study of the thermal system from 700 - 1000°K was made which found the Arrhenius relation:

$$k_1/k_1' = 1.44\ (\pm\ 0.05)\ \exp \left\{ (1500\ (\pm 50\ \text{cal/mol}^{\circ}\text{K})/RT) \right\}$$

The system was modeled using an RRKM Theory. The model was shown to fit the absolute rates in the pressure dependent region.

The observed branching ratio provides a "chemical clock" for the last excitation and decomposition events. At low pressures ($\leq$ 100 mtorr, $t_{collision} \geq 10^{-5.5}$ sec) the average decomposing molecule had an internal energy of 88 ± 6 kcal and decomposed in $10^{-9 \pm 0.5}$ sec. It thus absorbed its last photon in about 1 to 3 nanoseconds.

On studying the effects of pressure on this system we discovered the bimodal response to the laser pulse shape. A typical laser pulse has an intense, short peak (0.1μ sec) and a long, weaker tail (∼ 1 sec) each with about 1/2 the total energy. Each pumps at a different rate and produces a different energy population. At 30 torr Ne (or He) only the effects of the short peak are seen, the slowly pumped molecules in the tail being quenched by collisions before dissociation. The branching ratio R_p corresponding to this peak has an energy of 130 ± 15 kcal/mole and life-time of about $10^{-11 \pm 0.5}$ sec. The molecules absorbed their last photon in 10^{-11} sec and have experienced pumping and decomposition in a single mode pulse during a time of about 5 nanosec. To do this the energized molecule had to have an absorption cross-section about 100 times larger than the cross-section of room temperature molecules.

The discovery of isotopic branching as a chemical clock may provide an important new tool to laser scientists. It makes it possible to place intramolecular laser events on an absolute time scale and to begin to ask and answer questions about the time scale for the flow of energy in molecules, both large (> 6 atoms) and very large.

AFOSR Program Manager: William G. Thorpe, Major, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Ion-Molecule Reactions Involving Atmospheric Cluster Ions

2. PRINCIPAL INVESTIGATOR: Dr. Michael Henchman
Department of Chemistry
Brandeis University
Waltham, MA 02254

3. INCLUSIVE DATES: 1 February 1980 - 31 January 1981

4. GRANT NUMBER: AFOSR-80-0116

5. COSTS AND FY SOURCE: $9,998, FY80 (MINI GRANT)

6. PUBLICATIONS:

"The Isotope Exchange Reactions $H^+ + D_2 \rightleftarrows HD + D^+$ and $D^+ + H_2 \rightleftarrows HD + H^+$ in the Temperature Range 200-300K," M. J. Henchman, N. G. Adams, and D. Smith, J. Chem. Phys., 75, 1201 (1981).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

As a consequence of the discovery that the ergoneutral reaction between H_3O^+ and D_2O did not result simply in a proton transfer reaction to give H_2O and HD_2O^+ but gave products in which the hydrogens were found to be scrambled statistically, a general model that provides a unified treatment of proton transfer and hydrogen exchange reactions has been formulated. The model allows the systemization of a vast amount of experimental data on hydrogen exchange and proton transfer from many laboratories in terms of a common model which stresses that the processes occurring on the potential energy hypersurface are the same in each case. The successful use of reaction-coordinate diagrams to model proton transfer and hydrogen exchange reactions, has led to their application to reactions involving solvated ions. This led to the prediction that the ion H_3O^-, which had never been observed, could be prepared by colliding $OH^-.H_2O$ with H_2 at translational energies of around 10 eV. Experiments with the longitudinal tandem mass spectrometer at the Air Force Geophysics Laboratory showed unambiguously the formation H_3O^- although with an extremely small cross section, $10^{-19} cm^2$. The hydration energy of H^- was shown to be around 20 kcal mol^{-1}, in agreement with theoretical calculations of Dr. S. Guberman. This effort led to further collaborative efforts with an atmospheric research group at the University of Birmingham.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Energy Paths in Chemical Reactions

2. PRINCIPAL INVESTIGATOR: Professor George C. Pimentel
Chemistry Department
University of California
Berkeley, CA 94720

3. INCLUSIVE DATES: 1 October 1977 - 30 September 1981

4. GRANT NUMBER: AFOSR-78-3535

5. COSTS AND FY SOURCE: $76,987, FY78; $58,916, FY79; $102,213, FY80; $75,003, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. Leif Fredin
Dr. Heinz Frei
Dr. Stella Cesaro

7. JUNIOR RESEARCH PERSONNEL:

Eric Sirkin
S. Randolph Long
Yuan-Pern Lee
Robert Stachnik
Geraldine Richmond
Alvin Kennedy

8. PUBLICATIONS:

"Vibrational Populations in the $F+H_2$ Chemical Laser: V → V and V → R,T Energy Transfer Corrections," O. D. Krogh, D. K. Stone, and G. C. Pimentel, *J. Chem. Phys.*, *66*, 368 (1977).

"Chemiluminescence Reactions of Sulfur ($^3P_2$) Atoms in Cryogenic Matrices: $S+O_2 \rightarrow SO_2(\tilde{a}\ ^3B_1)$," S. R. Long and G. C. Pimentel, *J. Chem. Phys.*, *66*, 2219 (1977).

"ClF_x-H_2 Chemical Lasers (x=1,3,5): Vibration-Rotation Emission by HF from States with High Rotational Excitation," O. D. Krogh and G. C. Pimentel, *J. Chem. Phys.*, *67*, 2993-3001 (1977).

"Chemiluminescence of $SO(c'\,\Sigma^- \rightarrow a'\,\Delta)$ in Solid Argon," Y.-P Lee and G. C. Pimentel, *J. Chem. Phys.*, *69*, 3063-7 (1978).

"Chemical Reactions in Cryogenic Solids," G. C. Pimentel, *Berichte fur Physikalische Chemie*, *82*, 2(1978).

"HCO Production, Vibrational Relaxation, Chemical Kinetics, and Spectroscopy Following Laser Photolysis of Formaldehyde," J. P. Reilly, J. H. Clark, C. B. Moore, and G. C. Pimentel, J. Chem. Phys., 69, 4381-4394 (1978).

"Infrared Multiple Photon-Induced Molecular Elimination of HF from Fluorinated Olefins," AFOSR Report, April 1978.

"Chemiluminescence of S_2 in Solid Argon," Y.-P. Lee and G. C. Pimentel, J. Chem. Phys., 70, 692-698 (1979).

"Rotational Laser Emission by HF in the $ClF-H_2$ Chemical Laser," E. Cuellar and G. C. Pimentel, J. Chem. Phys., 71, 1385-1391 (1979).

"Diatomic Sulfur: Low Lying Bound Molecular Electronic States of S_2," W. G. Swope, Y.-P. Lee, and H. F. Schaeffer, III, J. Chem. Phys., 70, 947-953 (1979); "Sulfur Oxide; Low Lying Bound Molecular Electronic States of SO," ibid, 71, 3761 (1979).

"Vibrational Emission by HCl from the $ClF-H_2$ Chemical Laser," G. C. Pimentel and O. D. Krogh, J. Chem. Physics, 73, 120-125 (1980).

"Formic Acid Chemiluminescence from the Cryogenic Reaction Between Triplet Methylene and Oxygen," Y.-P. Lee and G. C. Pimentel, J. Chem. Phys., 74, 4851-4857 (1981).

"HF Rotational Laser Emission Through Photoelimination from Vinyl Fluoride and 1,1-Difluoroethene," E. R. Sirkin and G. C. Pimentel, J. Chem. Phys., 75, 604-612 (1981).

"Chemiluminescence of Ethylene in an Inert Matrix and the Probable Infrared Spectrum of Methylene," Y.-P. Lee and G. C. Pimentel, J. Chem. Phys., 75, 4241-4246 (1981).

"The Reaction of Nitric Oxide and Ozone in Cryogenic Matrices: Quantum Mechanical Tunnelling and Vibrational Enhancement," H. Frei and G. C. Pimentel, J. Phys. Chem., 85, 3355-3360 (1981).

"Vibrational Excitation of Ozone and Molecular Fluorine Reactions in Cryogenic Matrices," H. Frei, L. Fredin, and G. C. Pimentel, J. Chem. Phys., 74, 397-411 (1981).

"The Chemiluminescent Reactions $Ba+H_2O$ and $Ba+O_3$ in Solid Argon," S. R. Long, Y.-P Lee, O. D. Krogh, and G. C. Pimentel, J. Chem. Phys. (accepted for publication).

"HF Rotational Laser Emission: CO and CO_2 Enhancement of V→R Multiquantum Energy Transfer," E. R. Sirkin and G. C. Pimentel, J. Chem. Phys. (submitted for publication).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The purpose of this research was to clarify the factors that need to be understood to develop chemically pumped lasers operating on electronic, vibrational, or rotational transitions. Chemiluminescence from reaction products formed at very low temperatures (10-20°K) has provided an effective, though as yet only qualitative, way of detecting chemical pumping into excited electronic states. Using argon and nitrogen solids as host lattices, the method was pioneered using chemiluminescence from diatomic molecules O_2, S_2, and SO. Then it was extended to polyatomics, SO_2, C_2H_4, and HCOOH. Chemical pumping HF and HCl vibrational lasers by the reaction of H_2 with ClF, ClF_3, and ClF_5 was used to determine the vibrational rate constants into particular vibrational states. The ClF-H_2 reaction was also used to excite HF pure rotational laser emission. This study and a similar photoelimination-pumped rotational laser study showed that resonant vibration-to-rotation energy transfer plays an important role in the relaxation of vibrational population inversions in HF lasers.

A high energy, pulsed CO_2 laser was used to investigate the bimolecular chemistry of gaseous molecules containing high levels of vibrational excitation. Such multiphoton excitation of trifluoroethylene, for example, initiates chemistry attributable to difluorethylidine. Similar excitation of butadiene gives products that can be recognized as fragmentation products of butadiene dimers. Another type of experiment involved single photon vibrational excitation of reactions in cryogenic matrices. Using tuned infrared lasers as light sources and infrared detection, quantum yields could be measured for the F_2-ethylene reaction. Mode-specific reaction behavior was observed.

AFOSR Program Manager: William G. Thorpe, Major, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Study of Non-Radiating Species in Metal + Oxidant Chemiluminescent Flames

2. PRINCIPAL INVESTIGATOR: Dr. James Gary Pruett
Department of Chemistry
University of Pennsylvania
Philadelphia, PA 19174

3. INCLUSIVE DATES: 1 December 1978 - 1 June 1981

4. GRANT NUMBER: F49620-79-C-0023

5. COSTS AND FY SOURCE: $37,800, FY79; $45,800, FY80; $7,693, FY81

6. JUNIOR RESEARCH PERSONNEL:

Yen Chu Hsu
Gary White
Nick Furio

7. PUBLICATIONS:

"Lifetimes and Transition Moments Among Excited Electronic States of BaO," Yen Chu Hsu, Bruce Hegemann, and J. Gary Pruett, J. Chem. Phys., 72, 6437 (1980).

"Barium Oxide, the Questions Unanswered," R. W. Field, R. A. Gottscho, J. Gary Pruett, and J. J. Reuther, Proceedings of the YAMADA Conference on Free Radicals (1979).

"Nascent Metastable Products in the Reactions Ba + NO_2 and Ba + N_2O," Yen Chu Hsu and J. Gary Pruett, J. Chem. Phys. (accepted for publication).

"Pulsed Optical-Optical Double Resonance in BaO Using the Weak $A'^1\pi \leftarrow X^1\Sigma^+$ Transition as an Intermediate," Yen Chu Hsu and J. Gary Pruett, (manuscript in preparation, to be submitted J. Mol. Spect.).

"Rotational and Parity Relaxation in the $A'^1\pi$ State of BaO," Yen Chu Hsu and J. Gary Pruett, (manuscript in preparation, to be submitted to J. Chem. Phys.).

"Sub Doppler Optical-Optical Double Resonance Spectroscopy of BaO," R. A. Gottscho, P. S. Weiss, R. W. Field, and J. Gary Pruett, J. Mol. Spect., 82, 283 (1980).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The chemiluminescent reactions of Ba atoms with NO_2 and N_2O have provided a system in which to study reactive branching into detailed electronic, vibrational, and rotational states of the product BaO. The variety of low-lying excited electronic states of BaO has further provided the chance to directly investigate spin conservation effects in such reactions. The purpose of present research efforts has been to characterize the nascent product state distribution in the Ba + N_2O reactions and to provide detailed energy transfer rates among long-lived intermediate and reservoir states of importance to chemiluminescent emission. To accomplish these goals, some new spectroscopic analysis of previously uncharacterized excited states of BaO and development of techniques to observe laser induced fluorescence in chemiluminescent flames were necessary.

Studying the reactions first in a low pressure flow reactor, it was found that the Ba + N_2O reaction at 1 torr produced BaO ground state molecules with a thermal vibrational distribution of 3600°K, with population observed to v=30 of the ground state. Spectral features allowed vibrational characterization of the $C^1\Sigma^+$ state up to v=11, and a rough estimate of its radiative lifetime. Also observed were populations in the $A'^1\pi$, $b^3\pi$, and $a^3\Sigma$ states.

Subsequent work using optical-optical double resonance techniques established the $C^1\Sigma^+$ radiative lifetime as 10.5 nsec and measured absolute dipole transition moments of $\mu^2_{C-X} = 9.9\ D^2$, $\mu^2_{C-A} = 16.8\ D^2$, $\mu^2_{C-A_2{}^1} = 9.8\ D^2$, $\mu^2_{C-b} = 3.1\ D^2$, $\mu^2_{A-x} = 3.2\ D^2$ and $\mu^2_{A^1-x} = 14\ D^2$. Continued work using pulsed and time delayed optical-optical double resonance has mapped out several more excited electronic state levels and provided rotational relaxation rates in the $A'^1\pi$ state. It was also possible to study separately the two nearly degenerate Λ components of the $A'^1\pi$ state. It was found that rotational relaxation was nearly gas kinetic while parity changing collisions were an order of magnitude less probable.

The reactions Ba + N_2O and Ba + NO_2 were also studied under single collision molecular beam conditions. The dominant nascent products of both reactions were found to be non-emitting ground electronic state molecules. For Ba + N_2O, these molecules were highly vibrationally excited and isoenergetic with the low-lying excited electronic states of BaO, thus providing a non-emitting reservoir for collision-induced chemiluminescence. For the Ba + NO_2 reaction, some nascent production of the $A^1\Sigma^+$, $A'^1\pi$, and $b^3\pi$ states was found, but no production of the spin allowed $a^3\Sigma$ state was observed. Thus it is clear that neither energy accessibility nor spin conservation plays a dominant role in the reactive dynamics of this system.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Theory and Experiments on Chemical Dynamics and Chemical Instabilities

2. PRINCIPAL INVESTIGATOR: Professor John Ross
Department of Chemistry
Stanford University
Stanford, CA 94305

3. INCLUSIVE DATES: 1 December 1976 - 31 December 1981

4. GRANT NUMBER: AFOSR-81-0125

5. COSTS AND FY SOURCE: $68,089, FY77; $70,629, FY78; $73,960, FY79; $134,537, FY80; $91,340, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. H. Metiu
Dr. Itamar Procaccia
Dr. David J. Zvijac
Dr. Nathan Presser
Dr. Michael Collins
Dr. Ronald Lovett
Dr. J. F. Currie
Dr. Dina Gutkovitz-Krusin
Dr. Peter Richter
Dr. Shoichi Kai
Dr. Stefan C. Müller
Dr. Katherine Clark Hunt

7. JUNIOR RESEARCH PERSONNEL:

Dr. R. H. Burton
Dr. Carlos Vila

8. PUBLICATIONS:

"Symmetry Rules for Nonconcerted Reactions," H. Metiu, T. George, and J. Ross, Chem. Phys., 11, 259 (1975).

"Formation of Ensembles with Constraints of Coherence," Itamar Procaccia, Shaul Mukamel, and John Ross, J. Chem. Phys., 66, 5064 (1977).

"Stochastic Reduction for Dynamics of Reactions with Complex Formation," David J. Zvijac, Shaul Mukamel, and John Ross, J. Chem. Phys., 67, 2007 (1977).

"Stability and Relative Stability in Reactive Systems Far from Equilibrium. I. Thermodynamic Analysis," Itamar Procaccia and John Ross, J. Chem. Phys., 67, 5558 (1977).

"Stability and Relative Stability in Reactive Systems Far from Equilibrium. II. Kinetic Analysis of Relative Stability of Multiple Stationary States," Itamar Procaccia and John Ross, J. Chem. Phys., 67, 5565 (1977).

"Kinetics of Aerosol Formation in Irradiated Gaseous NO$_2$-SO$_2$ Mixtures," K. Iwamoto, N. Presser, and John Ross, J. Chem. Phys., 68, 663 (1978).

"On the Theory of Unimolecular Reactions: Applications of Mean First Passage Time to Reaction Rates," Itamar Procaccia, Shaul Mukamel, and John Ross, J. Chem. Phys., 68, 3244 (1978).

"Chemical Relaxation Pulses and Waves. Analysis of Lowest Order Multiple Time Scale Expansion," Michael Collins and John Ross, J. Chem. Phys., 68, 3774 (1978).

"Franck-Condon Factors in Studies of Dynamics of Chemical Reactions. IV. Nonadiabatic Collisions," David J. Zvijac and John Ross, J. Chem. Phys., 68, 4468 (1978).

"Kinetic Instabilities in First Order Phase Transitions," Ronald Lovett, Peter Ortoleva, and John Ross, J. Chem. Phys., 69, 947 (1978).

"Comment on Rate of Polymorphic Transformation Between Phases II and III of Hexachloroethane," Horia Metiu and John Ross, J. C. S. Faraday I, 74, 2750 (1978).

"Instability and Far-from-Equilibrium States of Chemically Reacting Systems," P. Hannusse, P. Ortoleva, and John Ross, Advances in Chemical Physics, 38, Ed. Stuart A. Rice, John Wiley and Sons, Inc. (1978) (pp. 317-361).

"Statistical Mechanics of Stationary States. I. Formal Theory," I. Procaccia, D. Ronis, M. A. Collins, I. Oppenheim, and J. Ross, Phys. Rev. A, 19, No. 3, 1290 (1979).

"Dynamics of Domain Walls in Ferrodistortive Materials. I. Theory," M. A. Collins, A. Blumen, J. F. Currie, and J. Ross, Phys. Rev. B, 19, No. 7, 3630 (1979).

"Dynamics of Domain Walls in Ferrodistortive Materials. II. Applications to Pb$_5$Ge$_3$O$_{11}$ and SbSI-Type Ferroelectrics," J. F. Currie, A. Blumen, M. A. Collins, and John Ross, Phys. Rev. B, 19, No. 7, 3645 (1979).

"Franck-Condon Theory of Chemical Dynamics. VI. Angular Distributions of Reaction Products," Carlos L. Vila, David J. Zvijac, and John Ross, J. Chem. Phys., 70, 5362 (1979).

"Rayleigh-Benard Instability in Nonreactive Binary Fluids. I. Theory," Dina Gutkowicz-Krusin, Michael A. Collins, and John Ross, Phys. Fluids, 22 (8), 1443 (1979).

"Rayleigh-Benard Instability in Nonreactive Binary Fluids. II. Results," Dina Gutkowicz-Krusin, Michael A. Collins, and J. Ross, Phys. Fluids, 22 (8), 1451 (1979).

"Statistical Mechanical Theory of the Kinetics of Phase Transitions," Horia Metiu, Kazuo Kitahara, and John Ross, Fluctuation Phenomena, Studies in Statistical Mechanics, Vol. VII, Eds. E. W. Montroll and J. L. Lebowitz, North Holland Publ. Co., (1979).

"Chemical Instabilities," Peter Richter, Itamar Procaccia, and John Ross, Advances in Chemical Physics, Vol. XLIII, Eds. I. Prigogine and Stuart A. Rice, John Wiley and Sons, Inc. (1980).

"Rayleigh-Benard Instability in n-Component Reactive Fluids," Dina Gutkowicz-Krusin and John Ross, J. Chem. Phys., 72, 3588 (1980).

"Molecular Beam Study of the Chemi-ionization Reaction: $Ba + Cl_2 \rightarrow BaCl^+ + Cl^-$," R. H. Burton, J. H. Brophy, and C. A. Mims, J. Chem. Phys., 73, 1612 (1980).

"Path Integral Solutions of Stochastic Equations for Nonlinear Irreversible Processes: The Uniqueness of the Thermodynamic Lagrangian," K. L. C. Hunt and John Ross, J. Chem. Phys., 75, 976 (1981).

"Dynamic Fluctuations in Optical Bistabilities," M. DelleDonne and P. Richter, Z. Phys. B, 42, 271 (1981).

"On the Path Integral Solution of the Fokker-Planck Equation for a System with Non-Conservative Forces," Frederick W. Wiegel and John Ross, Phys. Lett., 84A, 465 (1981).

"Control and Dissipation in Oscillatory Chemical Engines," Peter H. Richter, Paul Rehmus, and John Ross, Prog. Theor. Phys., 66, 385 (1981).

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research program focused on the theoretical and experimental study of chemical dynamics and chemical instabilities. The details of chemical reactions and dynamics are of importance in all applications of chemical reactions ranging from explosive to atmospheric processes. Chemical instabilities occur in systems far from equilibrium and highly nonlinear processes may take place, such as multiple stationary states, oscillations of chemical intermediates and macroscopic pattern formation. Examples of instabilities are found in flames, in chemistry and physics of the upper atmosphere, and in turbulent combustion processes. In chemical dynamics an extensive study was completed of the Franck Condon approximation in chemical kinetics which showed it to be useful for qualitative and frequently quantitative predictions of reaction cross sections, angular distributions and internal energy distributions of products. A molecular beam study was completed of the angular and translational energy distributions for the reaction $Ba + Cl_2 \rightarrow BaCl^+ + Cl^-$. In the area of statistical mechanics a stochastic theory of nucleation was formulated which led to a uniform derivation of both the Landau-Ginzberg equation and the Cahn-Hilliard equation used for the discussion of phase transitions. A theory of the dynamics

of domain walls in ferrodistortive materials was presented and compared with a large set of experiments. A study was initiated of the statistical mechanics of stationary states maintained by the presence of spatial gradients. This showed that the light scattering from such systems must reflect the asymmetry of those gradients. In the area of chemical instabilities the issue of stability and relative stability in reactive systems far from equilibrium was investigated and the necessary and sufficient conditions for marginal stability were presented. It was shown that kinetic instabilities may occur in first-order phase transitions and that inhomogeneous fluctuations in such systems lead to macroscopic pattern formation. Hydrodynamic instabilities were studied in connection with chemical reactions. Conditions were determined for the onset of both stationary and oscillatory convection. The presence of chemical reactions introduces a chemical boundary layer which affects the hydrodynamic (Benard) instability. Finally a CARS (coherent anti-Stokes Raman Scattering) system was constructed for the purpose of measuring chemical concentrations as a function of time and space necessary for further studies of chemical instabilities.

AFOSR Program Manager: William G. Thorpe, Major, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Experimental Studies of the State-to-State Chemical Dynamics of Reactions Involving Air Triatomics

2. PRINCIPAL INVESTIGATOR: Milo E. Whitson, Jr.
The Aerospace Corporation
P.O. Box 92957
Los Angeles, CA 90009

3. INCLUSIVE DATES: 1 June 1977 - 28 February 1981

4. GRANT NUMBER: AFOSR-77-3348 (Grant administered through University of Southern California, Los Angeles, CA 90007)

5. COSTS AND FY SOURCE: $46,735, FY77; $63,803, FY78; $67,000, FY80

6. SENIOR RESEARCH PERSONNEL:

R. R. Herm
R. Liang
B. J. Sullivan

7. JUNIOR RESEARCH PERSONNEL:

S. S. Goldberg
T. Sickler

8. PUBLICATIONS:

Planned submission to the Journal of Chemical Physics.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The first measurements of the full vibrational distribution of NO produced in the room temperature reaction

$$N(^4S) + O_2 \rightarrow NO\ (0 \leq v \leq 7) + O$$

were performed in this project. The technique of UV laser induced fluorescence detection of NO(v) was employed, which permitted observation of NO production under conditions where O_2 vibrational quenching of the NO(v) was insignificant. The technique permitted the first observation of NO(v=0) and NO(v=1) concentrations.

The relative ratios of $[NO(v)]/k_D{}^v$ were measured, where $k_D{}^v$ is the vibrationally dependent rate of NO removal by the reaction

$$N(^4S) + NO(v) \xrightarrow{k_D} N_2 + O.$$

Assuming the $k_D{}^v$ is independent of v, we calculate that the NO vibrational distribution ratios for $0 \leq v \leq 7$ are

57.8: 4.2: 5.7: 6.9: 5.8: 6.5: 6.6: 6.5,

expressed as % of total NO production. This result indicates that the $N(^4S) + O_2$ reaction produces 42% of the NO molecules in infrared-active states, 38% of them in levels ≥ 2. In terms of energy deposition, 28% of the 1.39 eV exothermicity of the reaction goes into $v \geq 2$; this is ∼ 3 times more than predicted by earlier studies.

The observed NO(v) ratios are in fact the nascent production ratios if vibrational relaxation of NO(v) by N atoms occurs with a rate much smaller than the rate of removal of NO(v) by reaction with N atoms. Assuming that N atom quenching is insignificant we calculate the set of rate coefficients K_1^v, for $0 \leq v \leq 7$, to be 52., 3.8, 5.1, 6.2, 5.2, 5.9, 5.9, 5.9 in units of 10^{18} cm^3 $molecule^{-1}$ sec^{-1}. If rapid N atom quenching occurs, production of infrared active states of NO by the $N(^4S) + O_2$ reaction is even more efficient than these rates indicate.

In addition to the development of laser induced fluorescence detection techniques for NO and the new kinetic data obtained, this work has identified key processes which must be understood before the results reported for the $N + O_2$ reaction, or calculations based on current radiance models can be fully accepted.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Alkaline Earth-Noble Gas Excimers

2. PRINCIPAL INVESTIGATOR: Dr. John J. Wright
Department of Physics
University of New Hampshire
Durham, NH 03824

3. INCLUSIVE DATES: 1 March 1979 - 31 August 1981

4. GRANT NUMBER: F49620-79-C-0049

5. COSTS AND FY SOURCE: \$46,735, FY79; \$27,060, FY80; \$11,276, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. L. C. Balling
Dr. M. D. Havey

7. JUNIOR RESEARCH PERSONNEL:

Paul Fletcher
Steve Frolking

8. PUBLICATIONS:

"$^1P_1 \rightarrow {}^3P_1$ Excitation Transfer for Ca and Sr with the Nobel Gases," J. J. Wright and L. C. Balling, J. Chem. Phys., 73, 1617 (1980).

"Experimental Potentials of the $X^2\Sigma^+$ and $A^2\Pi$ States of NaHe," M. D. Havey, S. E. Frolking, and J. J. Wright, Phys. Rev. Letters, 45, 1783 (1980).

"Experimentally Determined Potential Curves for the $X^2\Sigma^+$ and $A^2\Pi$ States of NaNe," M. D. Havey, S. E. Frolking, J. J. Wright, and L. C. Balling, accepted for publication in Phys. Rev.

"$A^2\Pi$ Potentials of LiHe and LiNe," J. J. Wright, M. D. Havey, and L. C. Balling, to be submitted for publication.

"Alkaline Earth-Noble Gas Excimers," J. J. Wright, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project was undertaken to investigate the interaction between alkaline earth atoms in the triplet state and noble gas atoms. A major effort was devoted to producing large triplet state populations via laser excitation of the singlet state and collisional transfer to the triplet state. Cross sections for this process were measured using a new technique developed in this laboratory. These cross sections were much larger than expected, probably due to molecular curve crossings with intermediate states. The results predicted a population inversion in strontium was possible and an attempt was made to produce a strontium laser. Because of low laser pump power, an inversion of only fifty percent was achieved where as lasing threshold required ninety percent. Attempts to observe far wing emission from calcium and strontium interactions with noble gases at high temperatures failed because of the thermal energies involved and because of blackbody radiation. A technique was developed to do laser spectroscopy at low temperatures in a sealed cell containing metal atom vapors and high pressure noble gases. The technique was tested by measuring, for the first time, the excited state potential of the sodium-helium excimer molecule. This difficult experiment was made possible by state of the art laser spectroscopy and the low temperature technique, which enhanced the excimer emission by orders of magnitude.

AFOSR Program Manager: William G. Thorpe, Capt, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: The State Identification of Reaction Products

2. PRINCIPAL INVESTIGATOR: Dr. Richard N. Zare
Department of Chemistry
Stanford University
Stanford, CA 94305

3. INCLUSIVE DATES: 1 July 1977 - 31 October 1981

4. GRANT NUMBER: AFOSR-77-3363

5. COSTS AND FY SOURCE: \$96,000, FY78; \$96,000, FY79; \$175,357, FY80
\$197,527, FY81

6. SENIOR RESEARCH PERSONNEL:

Dr. L. Wöste
Dr. F. Engelke
Dr. J. C. Whitehead
Dr. D. S. Perry
Dr. D. M. Rider
Dr. R. C. Estler
Dr. C. T. Rettner
Dr. J. Allison
Dr. Z. Karny

7. JUNIOR RESEARCH PERSONNEL:

D. R. Dickson
M. A. Johnson
A. Gupta

8. PUBLICATIONS:

"The Four-Centre Reaction $I_2 + F_2$ Studied by Laser-Induced Chemiluminescence in Molecular Beams," F. Engelke, J. C. Whitehead, and R. N. Zare, Faraday Disc. Chem. Soc., 62, 222 (1977).

"Determination of Absolute Photon Yields under Single-Collision Conditions," C. R. Dickson, S. M. George, and R. N. Zare, J. Chem. Phys., 67, 1024 (1977).

"Laser-Induced Chemiluminescence: Variation of Reactions Rate with Reagent Geometry," Ron C. Estler and Richard N. Zare, JACS 100, 1323 (1978).

"Effect of Vibrational Excitation on the Molecular Beam Reactions of Ca and Sr with HF and DF," Ziv Karny and Richard N. Zare, J. Chem. Phys., 68, 3360 (1978).

"Study of Excited Fragment Emission from the Electron Impact Dissociation of Volatile Mercury(II) Halides," J. Allison and R. N. Zare, Chem. Phys., 35, 263 (1978).

"Effect of Reagent Orientation and Rotation upon Product State Distribution in the Reaction Sr+HF(v=1,J) → SrF(v',J')+H," Ziv Karny, Ron C. Estler, and Richard N. Zare, J. Chem. Phys., 69, 5199 (1978).

"Laser-Induced Chemical Processes: Reactions with Oriented Reagents," Richard N. Zare, (K. L. Kompa and S. D. Smith - eds), in Laser-Induced Processes in Molecules, Springer Series in Chemical Physics, Vol. 6 (Springer Berlin, Heidelberg, New York), pp. 225-231 (1978).

"Kinetics of State-Selected Species," Richard N. Zare, Polanyi Memorial Lecture for Faraday Discussion No. 67, Faraday Discussions of the Chemical Society, No. 67, pp. 7-15 (1979).

"Laser-Induced Fluorescence Measurement of the Nascent Rotational Distribution of $N_2^+ (X^2 \Sigma_g^+)$ Formed by Electron Impact on N_2," J. Allison, T. Kondow, and R. N. Zare, Chem. Phys. Lett., 64, 202 (1979).

"Effect of Reagent Translation on the Dynamics of the Exothermic Reaction Ba+HF," Arunava Gupta, David S. Perry, and Richard N. Zare, J. Chem. Phys., 72, 6237 (1980).

"Comparison of Reagent Translation and Vibration on the Dynamics of the Endothermic Reaction Sr+HF," Arunava Gupta, David S. Perry, and Richard N. Zare, J. Chem. Phys., 72, 6250 (1980).

"Use of Lasers in the Study of the State-to-State Reaction Dynamics: Ba, Sr + HF," David S. Perry, Arunava Gupta and Richard N. Zare, Electro-Optic Laser '80, Proceedings, Industrial and Scientific Conference Management, Inc., Chicago, 1981.

"Origin of InI Emission in Laser Studies of the Crossed Beam Reaction In + I_2," Charles T. Rettner, Ludger Wöste and Richard N. Zare, Chem. Phys., 58, 371 (1981).

"Rotational Analysis of Congested Spectra: Application of Population Labeling to the BaI C-X System," Mark A. Johnson, Christopher R. Webster, and Richard N. Zare, J. Chem. Phys., 75, 5575 (1981).

General Discussion, J. Allison, M. A. Johnson, and R. N. Zare, Faraday Discuss. Chem. Soc., 67, 124 (1979).

"Molecular Beam Studies of the Reaction Dynamics of Ba + HF and Sr + HF," A. Gupta, Ph.D. Thesis, Stanford University (1980).

C. R. Dickson, Ph.D. Thesis, Columbia University (1976).

9 ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Efforts were continued to understand the dynamics of elementary chemical reactions using lasers to prepare the reagents in specific quantum states and to probe the state distribution of the reaction products. Attention has been concentrated on the bimolecular exchange reactions $M + HF \rightarrow MF + H$ where M is a group IIA metal atom (Ca, Sr, Ba).

Using an HF laser to excite the HF, measurements of state-to-state reaction rates for their reactions with Sr and Ca were made. The rate constants for reaction with HF ($v = 1$) are both found to be at least four orders of magnitude larger than for reactions with HF ($v = 0$). Furthermore, by making a seeded supersonic beam of HF ($v = 0$), it was possible to compare the relative effects of reagent translation and vibration on the dynamics of the reaction of Sr with HF. The cross section for the reaction with HF ($v = 1$) is found to be 1-10 times greater than for HF ($v = 0$) when the same total energy is supplied as reagent translation. Product internal energy distributions and total relative cross sections as a function of collisional energy are also measured. Most of these findings can be reproduced by a phase space model which suggests that the reaction may occur via multiple encounters.

It has also been possible to examine the effect of the HF ($v = 1$) orientation and rotation upon product state distribution for this reaction. Both broadside attack and increasing rotational energy are found to favor higher vibrational excitation of the SrF product. It is believed that these results provide evidence for a bent approach geometry.

In two other studies, examination was made of the exothermic reactions of Ba + HF and $In + I_2$. While the first of these is found to channel more than half the available energy into reagent translation, the latter channels a similar fraction into InI vibration. These findings are consistent with indirect and direct mechanisms, respectively, for the two reactions. The $In + I_2$ study was particularly important as it served to demonstrate that the InI^* emission observed in an earlier study results from laser-induced fluorescence of InI, not from the laser-induced chemiluminescent reaction $In + I_2^* \rightarrow InI^* + I$.

Finally, the laser-induced fluorescence technique was applied to the study of molecular ions of aeronomic importance. In the first experiments, $N_2^+(X^2\Sigma_g^+)$ was produced by electron impact. It was found that this species could be sensitively detected as a function of its (v,J) quantum state. Analysis of the $B^2\Sigma_u^+ - X^2\Sigma_g^+$ (0,0) band revealed that the rotational distribution of the N_2^+ could be characterized by a temperature which increases slightly with decreasing electron impact energy. Currently, this work is being extended to studies of the CO_2^+ ion.

AFOSR Program Manager: William G. Thorpe, Major, USAF

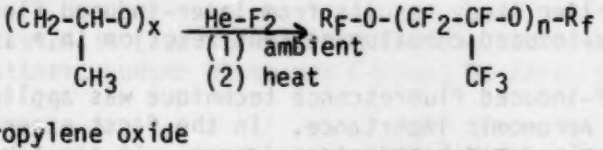
RESEARCH IN FLUOROCHEMICAL SYNTHESIS

Dr. Anthony J. Matuszko

The AFOSR program in chemical reactivity and synthesis includes a few research efforts in fluorine chemistry which have produced new and unique approaches to the synthesis of fluorocarbon derivatives and other fluorine containing compounds. Among these are included research at the University of Texas on utilization of a direct fluorination technique for the synthesis of previously unattainable compounds, the synthesis for the first time at Ultrasystems of phosphatriazines with fluorocarbon ether side groups, and work performed at the University of Iowa on new ways of making functional fluorocarbon compounds.

At MIT and more recently at the University of Texas, Professor Richard Lagow and his research group have been improving on procedures for direct fluorination first carried out by Lagow and Margrave at Rice University in the late 1960's. The procedures involve very precise control of fluorine concentration during the reaction and initial high dilution of the elemental fluorine with helium. (See Progress in Inorganic Chemistry, 26, 161 (1979) for a summary of the direct fluorination work.) All sources of oxygen and water must be removed from the fluorination system. Fluorination reactions have been run at cryogenic, room, and elevated temperatures, depending on the reactant to be fluorinated and the stability of the products which are formed.

Perfluoropolyethers have been successfully synthesized by way of direct fluorination of polymethylene oxide, polyethylene oxide, and polypropylene oxide. The reactions are first run at room temperature followed by further fluorination at elevated temperature. (J. Chem. Soc., Perkin Transactions, 1321 (1981).



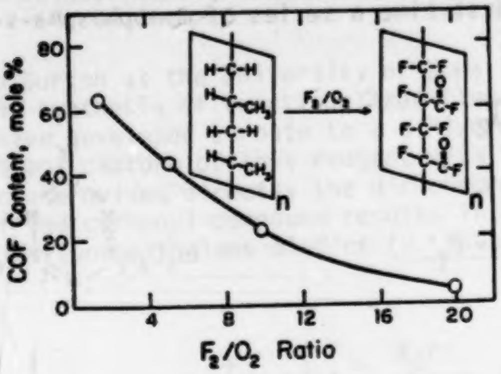
$$(CH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-O)_x \xrightarrow[\substack{(1)\ \text{ambient}\\(2)\ \text{heat}}]{He-F_2} R_F-O-(CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}}-O)_n-R_f$$

polypropylene oxide

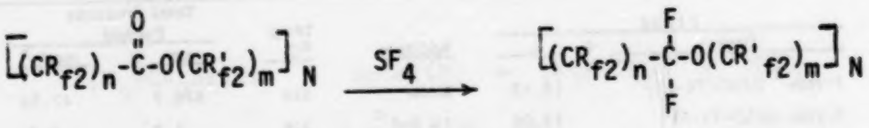
where $R_F = CF_3,\ C_2F_5,\ n\text{-}C_3F_7$

Simultaneous fluorination and functionalization of hydrocarbon polymers was accomplished by Lagow by introducing a low concentration of oxygen with the fluorine in the direct fluorination of polypropylene. (J. Amer. Chem. Soc., 100, 1948 (1978).

The relationship between oxygen introduced and the COF content (polypropylene)

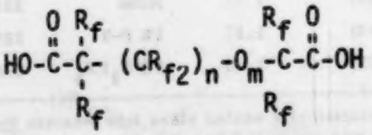


Recently, a new general synthesis for perfluoropolyethers was developed in Lagow's laboratory. The unique advantage of this new synthetic technique is that it makes possible the synthesis of very highly branched polyethers which is not possible using the conventional polymerization technology. In the process carboxylic acid substituted difunctional perfluoropolyethers are easily obtained. The process involves first preserving ester linkages during direct fluorination at low temperatures. The resulting perfluoropolyester oligomers are then treated with sulfur tetrafluoride to convert the ester carbonyl groups to CF_2 groups, thus rendering a perfluoropolyether.



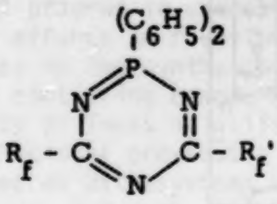
$$\left[(CR_{f2})_n-\overset{O}{\overset{\|}{C}}-O(CR'_{f2})_m\right]_N \xrightarrow{SF_4} \left[(CR_{f2})_n-\underset{F}{\overset{F}{C}}-O(CR'_{f2})_m\right]_N$$

When nonstoichiometric amounts of SF_4 are used there is left in the structure a number of unreacted ester linkages. The systems are then hydrolyzed (perfluoroesters hydrolyze spontaneously) to produce difunctional perfluorocarbon ether diacids.

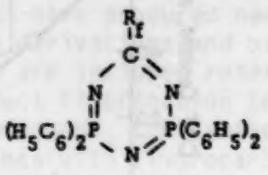


$$HO-\overset{O}{\overset{\|}{C}}-\underset{R_f}{\overset{R_f}{C}}-(CR_{f2})_n-O_m-\underset{R_f}{\overset{R_f}{C}}-\overset{O}{\overset{\|}{C}}-OH$$

As reported briefly in the 23rd AFOSR Chemistry Program Review, Dr. Kay Paciorek and her research group at Ultrasystems in Irvine, California, synthesized for the first time a series of monophospha-s-triazines and diphospha-s-triazines.



monophospha-s-triazine



diphospha-s-triazine

The successful synthesis of these phosphatriazines was in itself a significant accomplishment. In addition, several derivatives of these newly made compounds containing fluorocarbon ether side groups have been found to be effective as anticorrosion and antioxidation additives for various fluorocarbon ether fluids (Krytox, Fomblin Z, Freon-E) tested for high temperature applications. (Progress Report to AFOSR, 15 Oct 1981).

COMPARISON OF ADDITIVES' ACTION ON PERFLUOROALKYLETHER FLUIDS IN THE PRESENCE OF M-50 ALLOY AT ELEVATED TEMPERATURES IN OXYGEN OVER A 24 HR PERIOD[a]

Fluid				Total Products Formed	
Type	g	Additive	Temp °C	mg	mg/g[b]
Krytox[2] (MLO-71-6)	12.13	None	316	576.7	47.54
Krytox (MLO-71-6)	13.28	1% P-3[c]	316	3.3	0.2
Krytox[2] (MLO-71-6)	8.59	1% C_2PN_3[d]	316	6.1	0.7
Fomblin Z[8] (MLO-72-22)	4.24	None	316	total degradation	
Fomblin Z[8] (MLO-72-22)	4.08	1% P-3	316	1176.2	288.3
Fomblin Z[8] (MLO-72-22)	3.39	1% C_2PN_3	316	535.1	157.8
Fomblin Z[8] (MLO-72-22)	3.34	None	288	1117.1	421.6
Fomblin Z[8] (MLO-72-22)	3.34	1% C_2PN_3	288	1.1	0.3
Fomblin Z[8] (MLO-72-22)	3.57	1% P-3	288	3.4	0.9
Freon E-7 (ELO-66-55)	1.16	None	288	1215.1	1047.5
Freon E-7 (ELO-66-55)	1.21	1% P-3	288	23.5	19.9
Freon E-7 (ELO-66-55)	1.10	1% C_2PN_3	288	17.0	15.5

a) The apparatus consisted of a sealed glass tube wherein the metal coupon was suspended in the fluid; the test was conducted in pure oxygen; at the conclusion of the test, the products were collected and measured.

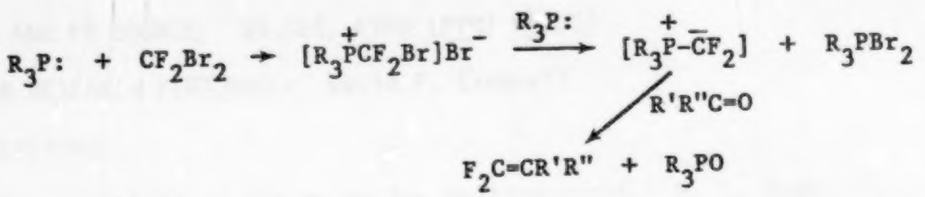
b) Products formed in mg/g of fluid used.

c) $[C_3F_7OCF(CF_3)CF_2OCF(CF_3)CF_2(C_6F_4)]_3P$.

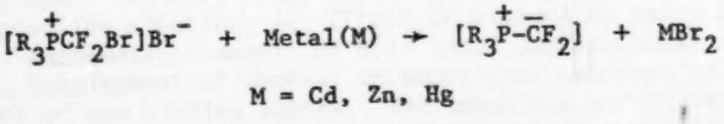
d) 1-diphenylphospha-3,5-bis$[C_3F_7OCF(CF_3)CF_2OCF(CF_3)]$-2,4,6-triazine.

The Ultrasystems research group is currently working on the synthesis of higher molecular weight fluorocarbon ether substituted phosphatriazine elastomers.

Professor Donald Burton at the University of Iowa is looking at new approaches to the synthesis of functionalized fluorocarbons. He and his research group have developed a route to a difluoromethylene Wittig type reagent. Subsequent capture of this reagent with the appropriate aldehyde or ketone provides directly the difluoromethylene olefin. Proper choice of the carbonyl compound results in the preparation of a wide variety of difluoromethylene olefins (J. Fluorine Chem., 18, 323-356 (1981).

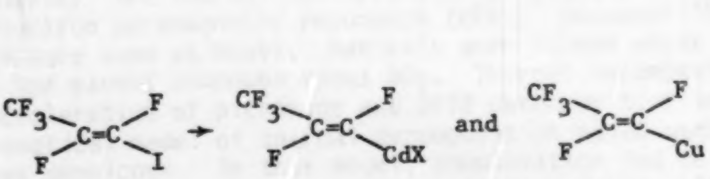

$$R_3P: + CF_2Br_2 \rightarrow [R_3\overset{+}{P}CF_2Br]Br^- \xrightarrow{R_3P:} [R_3\overset{+}{P}-\overset{-}{C}F_2] + R_3PBr_2$$
$$[R_3\overset{+}{P}-\overset{-}{C}F_2] \xrightarrow{R'R''C=O} F_2C=CR'R'' + R_3PO$$

Since reactive fluoroolefins react rapidly with tertiary phosphines, in many cases the Wittig dehalogenation reaction cannot be used as a route to fluoroolefins. Professor Burton and his research group have developed alternative preparative routes for these compounds through dehalogenation of the bromodifluoromethyl triphenylphosphonium bromide with active metals.


$$[R_3\overset{+}{P}CF_2Br]Br^- + \text{Metal(M)} \rightarrow [R_3\overset{+}{P}-\overset{-}{C}F_2] + MBr_2$$
$$M = Cd, Zn, Hg$$

A preliminary report on this work has been published. (J. Fluorine Chem., 18, 293-298 (1981).

In one other phase of his research, Professor Burton has been able to generate vinylic cadmium and copper reagents stereospecifically from the corresponding vinylic halide.



The work is still in the exploratory stage, but preliminary results indicate that the reagents are quite stable at room temperature, can be prepared on a large scale without difficulty, and permit one to carry out regiospecific and stereospecific reactions.

This summary is only a sampling of the achievements under the AFOSR program in fluorocarbon chemistry. The results will be of benefit to the Air Force long range program in the area of developing improved high temperature elastomers, fluids, fluid additives, and lubricants. Other AFOSR supported work not covered in this report includes research on synthesis and properties of novel inorganic fluorine compounds. The accomplishments in this phase of the synthesis program will be covered at a later date.

COMPLETED PROJECT SUMMARY

1. TITLE: Model Studies of Energetic Compounds

2. PRINCIPAL INVESTIGATOR: Professor W. Robert Carper
Department of Chemistry
Wichita State University
Wichita, Kansas 67208

3. INCLUSIVE DATES: 1 Feb 1980 - 30 Jan 1981

4. GRANT NUMBER: AFOSR-80-0104

5. COSTS AND FY SOURCE: $9,764, FY80 (MINI GRANT)

6. JUNIOR RESEARCH PERSONNEL: David P. Campbell

7. PUBLICATIONS:

"Thermal Decomposition of RDX Below the Melting Point," H. L. Pugh, L. P. Davis, J. S. Wilkes, W. R. Carper, and R. C. Dorey, Proc. Seventh Int. Sympos. on Detonation, 1981 O.N.R. (to be published).

"Model Studies of Energetic Compounds," W. Robert Carper, Final Technical Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A. Objectives: The objectives of this study were both long range and immediate in scope. The long range objectives included: (1) Knowledge of thermal decomposition kinetics; (2) Effect of binders on aging mechanisms; (3) Development of mathematical models of both ideal and non-ideal detonation phenomena; (4) Development of thermal decomposition mathematical models; and (5) Development of new binding agents. The immediate objectives of this study included: (1) Determination of the mode of thermal decomposition of DATB and TATB and the identification of the molecular species produced; (2) Evaluation of the induction periods and energies of activation associated with the thermal decomposition of DATB and TATB ; and (3) Determination of binder properties of TNB by studying the DATB-TNB and TATB-TNB molecular complexes by stop-flow and static UV methods.

B. Accomplishments: The thermal decomposition of picramide and DATB was monitored by electron paramagnetic resonance (EPR). Hexamethylbenzene and diethyl adipate were used as hosts. Radicals were formed whose composition was similar to the parent compound minus NO_2. Thermal decomposition studies indicated an acceleration of picramide and DATB decomposition in TNT vs. TNB. A general mathematical model of thermal decomposition based upon binder complexation was developed. In this model, complexation led to radical formation, followed by termination and polymerization steps. In addition, three general schemes of radical formation were derived and one of these confirmed in preliminary experiments.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Picosecond Laser Studies of Excited State Proton Transfer

2. PRINCIPAL INVESTIGATOR: Professor Kenneth B. Eisenthal
Department of Chemistry
Columbia University
New York, New York 10027

3. INCLUSIVE DATES: 1 September 1977 - 30 September 1980

4. GRANT NUMBER: AFOSR-77-3407

5. COSTS AND FY SOURCE: $56,174, FY77; $57,000, FY78; $84,500, FY79

6. SENIOR RESEARCH PERSONNEL:

Dr. K. Gnadig	Dr. Y. Wang
Dr. W. M. Hetherington III	Dr. R. H. Micheels
Dr. G. M. Korenowski	Dr. C. A. Langhoff

7. JUNIOR RESEARCH PERSONNEL:

M. K. Crawford	S. Y. Hou
C. Dupuy	M. J. McAuliffe

8. PUBLICATIONS:

"Picosecond Laser Studies of Electron-Hole Interactions and Double Proton Transfer," K. Gnädig, W. Hetherington, M. Crawford, R. Micheels and K. B. Eisenthal, Picosecond Phenomena, eds. C. V. Shank, E. P. Ippen, and S. L. Shapiro, Springer-Verlag, 1978.

"Picosecond Dynamics of Double Proton Transfer in 7-Azaindole Dimers," W. M. Hetherington III, R. H. Micheels, and K. B. Eisenthal, Chemical Physics Letters, 66, 230 (1979).

"Intramolecular Proton Transfer and Energy Relaxation in Ortho-Hydroxybenzophenone," S. Y. Hou, W. M. Hetherington III, G. M. Korenowski, and K. B. Eisenthal, Chemical Physics Letters, 68, 282 (1979).

"Picosecond Laser Studies of the Photodissociation of I_2-Aromatic Complexes in Solution," C. A. Langhoff, K. Gnädig and K. B. Eisenthal, Chemical Physics Letters, 46, 117 (1980).

"Picosecond Laser Studies of Electron Solvation in Alcohols," Y. Wang, M. K. Crawford, M. J. McAuliffe, and K. B. Eisenthal, Chemical Physics Letters, 74, 160 (1980).

"Intramolecular Excited-State Charge-Transfer Interactions and the Role of Ground-State Conformations," Y. Wang, M. K. Crawford, and K. B. Eisenthal, Journal of Physical Chemistry, 84, 2696 (1980).

"Dynamics and Energetics of the Singlet-Triplet Interconversion of Diphenylcarbene," K. B. Eisenthal, N. J. Turro, M. Aikawa, J. A. Butcher, Jr., C. Dupuy, G. Hefferon, W. Hetherington, G. M. Korenowski, and M. J. McAuliffe, Journal of the American Chemical Society, 102, 6563 (1980).

"Intermediates and Charge Transfer Phenomena in Liquids," M. K. Crawford, C. Dupuy, W. Hetherington, G. Korenowski, M. J. McAuliffe, Y. Wang, and K. B. Eisenthal, in Picosecond Phenomena II, eds. R. M. Hochstrasser, W. Kaiser, C. V. Shank, Springer-Verlag, 1980.

"Photodissociation of Diphenyldiazomethane and Energy Relaxation in the Diphenylcarbene Fragment," C. Dupuy, G. M. Korenowski, M. McAuliffe, W. Hetherington, and K. B. Eisenthal, accepted for publication by Chemical Physics Letters.

"Picosecond Laser Studies of Excited State Proton Transfer," Kenneth B. Eisenthal, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A primary objective of this research has been the development and application of picosecond laser methods to the study of ultrafast molecular processes in liquids. Using the techniques of picosecond spectroscopy we have obtained new information on the physical and chemical pathways by which molecules in excited electronic states dissipate their electronic energy; intramolecular and intermolecular motions in liquids; and the properties of short-lived fragments generated by the laser photoexcitation of the original ground state molecules.

In particular we have investigated: (1) the role of excited state proton transfer in the photostability of orthohydroxybenzophenone and in the tautomerization of 7-azaindole dimers, (2) intramolecular motions and electron transfer in hooked together donor and acceptor molecules, (3) photodissociation of iodine, I_2, complexed with aromatic molecules, the subsequent iodine atom reaction with aromatic molecules, and cage effects; (4) photodissociation of diphenyldiazomethane and energy relaxation in the important chemical intermediate, diphenylcarbene and (5) photodissociation of pyrene in alcohols, the solvation dynamics of the ionized electron, and insight provided by this work on energy deposition in pulse radiolysis experiments. We have used picosecond fluorescence, laser-induced fluorescence and a new technique combining a laser-triggered flash lamp with a streak camera to obtain transient absorption with picosecond resolution, extending for nanoseconds, in one firing of the laser.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Solute-Gas Equilibria in Multi-Organic Aqueous Systems

2. PRINCIPAL INVESTIGATOR: Dr. James Gossett
Environmental Engineering Department
Cornell University
Ithaca, NY 14853

3. INCLUSIVE DATES: 1 January 1981 - 30 September 1981

4. GRANT NUMBER: AFOSR-81-0074

5. COSTS AND FY SOURCE: $9,993, FY81 (MINI GRANT)

6. PUBLICATIONS:

"Solute-Gas Equilibria in Multi-Organic Aqueous Systems," James M. Gossett, Final Technical Report.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The objective of this research was to study the effects of temperature, ionic strength, and presence of additional organics on the aqueous solution/gas equilibria of a variety of chlorinated organic compounds: 1,1,1-trichloroethane, tetrachloroethylene, trichloroethylene, chloroform, methylene chloride, and o-dichlorobenzene. Henry's constant for each alone was determined in pure water over the temperature range, 10^0-30^0 C, using an equilibrium, batch stripping reactor. Data were fit to a regression equation.

Henry's constants for selected organic solvents were determined at ionic strengths up to 1.0 M (KCl). Results suggest that ionic strength effects on activity can be ignored in systems possessing ionic strengths less than 0.07 M.

Henry's constants for organic solvents dissolved in multi-component aqueous mixtures of other organic solvents were measured. It was found that relatively small concentrations of the organic solvents in water mutually affected one another's volatility.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: A Search for New Fuel Components in Explosive Mixtures with Ammonium Nitrate

2. PRINCIPAL INVESTIGATOR: Dr. Maurice C. Neveu
Department of Chemistry
State University College of New York
Fredonia, NY 14063

3. INCLUSIVE DATES: 1 May 1980 - 30 April 1981

4. GRANT NUMBER: AFOSR-80-0134

5. COSTS AND FY SOURCE: $9,963, FY80 (MINI GRANT)

6. PUBLICATIONS:

"A Search for New Fuel Components in Explosive Mixtures with Ammonium Nitrate," Maurice C. Neveu, Final Technical Report.

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The primary objective of this study was the finding of new fuel components in fuel/oxidizer intermolecularly reacting explosive systems. For more effective explosive properties it was desired to find fuels which would form eutectic mixtures with the oxidizer, ammonium nitrate. An extensive series of dyes of known structure was screened for this desired characteristic by differential scanning calorimetry (DSC). Thirteen of these formed eutectic mixtures with ammonium nitrate and showed a rapid exothermic reaction in this mixture. The significance of the use of dyes as fuel components in these systems and the possibility of using them to formulate a wide spectrum of explosive properties is discussed. A secondary objective, the synthesis of 2,2'4,4',6,6'-hexanitro-3,3'-biphenol and the study of its thermal properties as well as those of its potassium and ammonium salts, was also accomplished.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Basic Studies Relative to the Syntheses of Unsymmetrical Dimethylhydrazine and Monomethylhydrazine by Chloramination

2. PRINCIPAL INVESTIGATOR: Professor Harry H. Sisler
Department of Chemistry
University of Florida
Gainesville, FL 32611

3. INCLUSIVE DATES: 1 September 1975 - 30 June 1981

4. GRANT NUMBER: AFOSR-76-2915; AFOSR-80-0007

5. COSTS AND FY SOURCE: $41,237, FY76; $45,234, FY77; $60,000, FY78; $44,979, FY79; $72,142, FY80

6. SENIOR RESEARCH PERSONNEL:

Dr. Sampat R. Jain
Dr. Roy W. King
Dr. Milap A. Mathur
Dr. Lee Morganthaler

7. PUBLICATIONS:

"Chloramination of Trimethylhydrazine," Thomas J. Giordano and Harry H. Sisler, Inorganic Chem., 16, 2043 (1977)

"Pyrolysis and Hydrolysis of 2,2-Dimethyltriazanium Chloride," Milap A. Mathur, Harry H. Sisler, and Lee N. Morganthaler, Inorganic Chem., 18, 2350 (1979).

"Formation of Dimethylmercury in the Oxidation of Methylhydrazine by Mercuric Oxide," Harry H. Sisler, Milap A. Mathur, Sampat R. Jain, and Roy W. King, J. Org. Chem., 45, 1329 (1980).

"Synthesis of Methylhydrazine in Nonaqueous Solvents," Sampat R. Jain, Milap A. Mathur, and Harry H. Sisler, Inorganic Chem., 19, 2192 (1980).

"Synthesis of Methylhydrazine and 1,1-Dimethylhydrazine by the Reactions of Hydroxylamine-O-Sulfonic Acid with Methyl- and Dimethylamine," Harry A. Sisler. Milap A. Mathur, and Sampat R. Jain, Inorganic Chem., 19, 2846 (1980).

"Oxidation of 1,1-Dimethylhydrazine by Oxidation," submitted for publication.

"Studies of Chloramination of Dimethylamine and 1,1-Dimethylhydrazine," submitted for publication.

"Basic Studies Relative to the Syntheses of Unsymmetrical Dimethylhydrazine and Monomethylhydrazine by Chloramination," Harry H. Sisler, Final Technical Report (1980).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Unsymmetrical dimethylhydrazine (UDMH) and monomethylhydrazine (MMH) have achieved special importance as high energy rocket and space shuttle fuels. These compounds have large heats of combustion, relatively high densities and high specific impulses. Until the mid 1970's, UDMH was manufactured by the catalytic hydrogenation of 1,1-dimethylnitrosamine (NDMA). Studies showed that NDMA was highly carcinogenic. A search for a new manufacturing process drew attention to an earlier publication of Sisler and co-workers which reported the formation of substituted hydrazines by the chloramination of amines. In order to investigate the utility of the work of Sisler and co-workers for the production of UDMH and MMH, a joint project was undertaken in the fall of 1975 by the Chemical Laboratory at the University of Florida, Gainesville, Florida, and the Surface Weapon Center White Oak Laboratory, Silver Spring, Maryland.

The chloramination of dimethylamine in a solution of KOH in n-butanol was carried out in the presence of NH_3 at room temperature. The major products were 1,1-dimethylhydrazine, the dimethylhydrazone of formaldehyde, and 1,1,4,4-tetramethyl-2-tetrazene. Mechanisms for the formation of the various oxidation products were proposed.

The reaction of chloramine with trimethylhydrazine, $(CH_3)_2NNH(CH_3)$, was investigated. The principal product formed when this reaction was carried out in ether was the dimethylhydrazone of formaldehyde, $(CH_3)_2NN{=}CH_2$. The absence of 1,2,2-trimethyltriazanium chloride, the expected product, was explained in terms of the weaker nucleophilicity of trimethylhydrazine compared to that of 1,1-dimethylhydrazine, which reacts with chloramine to form 2,2-dimethyltriazanium chloride.

The study of the oxidation of 1,1-dimethylhydrazine in solutions in diethyl ether or cyclohexane was carried out between 20 and 30° C. The principal product of this oxidation reaction under these conditions is formaldehyde dimethylhydrazone. Among the other products identified were water, 1,1,4,4-tetramethyl-2-tetrazene, nitrogen, methane, ammonia, formaldehyde monomethylhydrazone, sym. hexahydro-1,4-dimethyltetrazine, and N-dimethylnitrosamine.

Virtually no reaction takes place between chloramine and methylamine in ether, xylene, methanol, or diglyme solutions. Monomethylhydrazine can, however, be synthesized in appreciable yield in various media when chloramination is carried out in the presence of a fixed base such as potassium hydroxide or sodium methoxide.

In an attempt to prepare symmetrical dimethyl-2-tetrazene by the oxidation of monomethylhydrazine with yellow mercuric oxide, a byproduct hitherto unreported for mercuric oxide oxidations of methyl substituted hydrazines, viz., the highly toxic dimethylmercury, was obtained. It is suspected that this compound may be formed in the mercuric oxide oxidations of other methyl substituted hydrazines, Researchers should be aware of the considerable hazard associated with this possibility.

Preliminary investigations showed that chloramine, free of ammonia, dissolved in ether, reacts with an aqueous solution of monomethylurea to yield a complex mixture of monomethylhydrazine and its oxidation products, including the monomethylhydrazone of formaldehyde and methanol and other substances. 1,1-Dimethylhydrazine was also obtained. Similar results were obtained when an ethanol solution of ammonia-free chloramine was allowed to react with an aqueous solution of monomethylurea.

The synthesis of monomethylhydrazine was successfully achieved by reacting solutions of hydroxylamine-O-sulfonic acid with methylamine in diglyme. The synthesis of 1,1-dimethylhydrazine was carried out in a similar manner with dimethylhydrazine. A mechanism for the formation of formaldehyde dimethylhydrazone by the reaction of dimethylamine and chloramine was proposed. A study was conducted on the oxidation of monomethylhydrazine and 1,1-dimethylhydrazine by oxygen.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Synthesis of New Inorganic and Organometallic Materials

2. PRINCIPAL INVESTIGATOR: Profesor F. Gordon A. Stone
Department of Inorganic Chemistry
The University of Bristol
Bristol BS8 1TS UK

3. INCLUSIVE DATES: 1 October 1976 - 31 March 1981

4. GRANT NUMBER: AFOSR-76-3102

5. COSTS AND FY SOURCE: \$12,210, FY7T; \$12,210, FY77; \$13,500, FY79; \$16,900, FY80

6. SENIOR RESEARCH PERSONNEL:

Dr. G. K. Barker
Dr. J. L. Davidson

7. JUNIOR RESEARCH PERSONNEL:

N. M. Boag	J. Z. Nyathi
L. J. Farrugia	R. F. D. Stansfield
P. Mitrprachachon	M. J. Winter

8. PUBLICATIONS:

"Syntheses Involving Co-ordinatively Unsaturated Cyclopent dienylmolybdenum and -tungsten Complexes. Molecular and Crystal Structures of

$[\overline{\mathrm{Mo.C(CF_3)\colon C(CF_3).C}}\mathrm{{}_5H_5(CF_3C_2CF_3)(\eta\text{-}C_5H_5)}]$,"
J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc., Dalton Trans.*, *287*, (1977).

"Reactions of Low-valent Metal Complexes with Fluorocarbons. Bis (η -cyclo-octa-1,5-diene)-platinum and -palladium with Fluoroolefins," M. Green, A. Laguna, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc.*, *Dalton Trans.*, 1010 (1977).

"The Reaction of Bis(triethylphosphine)platinum and Pentakis(t-butyl isocyanide)ruthenium with Dicarba-*nido*-hexaboranes (8): Molecular Structures of $[\textit{nido}\text{-}\mu_{4,5}\text{-}\{\textit{trans}\text{-}(\mathrm{Et_3P})_2\mathrm{Pt}\overline{(\mathrm{H})\}\mu}\ 5,6\text{-}\mathrm{H}\text{-}2,3\text{-}\mathrm{C_2B_4H_6}]$, $[\textit{closo}\text{-}1,1\text{-}(\mathrm{Et_3P})_2\text{-}2,3\text{-}\mathrm{Me_2}\text{-}1,2,3\text{-}\mathrm{PtC_2B_4H_4}]$ and $[\mathrm{RuH(Bu^tNC)_5}]$ $[\textit{nido}\text{-}2,3\text{-}\mathrm{Me_2}\text{-}2,3\text{-}\mathrm{C_2B_4H_5}]$," G. K. Barker, M. Green, T. P. Onak, F. G. A. Stone, C. B. Ungermann, and A. J. Welch, *J. Chem. Soc.*, *Chem. Commun.*, 169 (1978).

"Formation of η^3-Bonded Lactone Complexes and Eight-membered Ring Metallacycles with Ketene Groups by the Insertion of Acetylenes into Carbon-Molybdenum and -Tungsten σ-Bonds; Molecular and Crystal Structures of Carbonyl (η-cyclopentadienyl)(3-5-η-2,3-dihydro-3,4,5-trimethyl-2-oxo-3-furyl)(t-butyl isocyanide)molybdenum and Carbonyl-(η-cyclopentadienyl)(3-4:5-6-η-2,3,4,5-tetramethyl-6-oxo-1-trifluoromethylhexa-1,3,5-trienyloxo)molybdenum," M. Green, J. Z. Nyathi, C. Scott, F. G. A. Stone, A. J. Welch, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 1067 (1978).

"Formation of Tetra- and Tri-nuclear Nickel Acetylene Complexes; Crystal and Molecular Structures of $[Ni_4(CO)_4\{\mu_3-(\eta^2-CF_3C_2CF_3)\}_3]$ and $[Ni_3(CO)_3\{\mu_3-(\eta^8-C_8H_8)\}\{\mu_3-(\eta^2-CF_3C_2CF_3)\}]$ with Evidence for a Nickel Stabilized Cyclo-octa-tetraene Dication," J. L. Davidson, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc.*, *Dalton Trans.*, 506 (1979).

"Oxidative-insertion Reactions of Zerovalent Nickel and Platinum Complexes with 1.7-Dicarba-*closo*-octaborane, 4,5-Dicarba-*closo*-nonaborane, and 1,6-Dicarba-*closo*-decarborane and Their C-Methyl Derivatives," M. Green, J. L. Spencer, and F. G. A. Stone, *J. Chem. Soc.*, *Dalton Trans.*, 1679 (1979).

"Insertion of Zerovalent Platinum Species in Bridging Boron-hydrogen-Boron Bonds of 2,3-Dicarba-*nido*-hexaborane (8), 2.3-Dimethyl-2,3-dicarba-*nido*-hexaborane (6) and Monocarba-*nido*-hexaborane (9); Molecular and Crystal Structure of $[nido-\mu_{4,5}-\{trans-(Et_3P)_2Pt(H)\}-\mu_{5,6}-H-2,3-C_2B_4H_6]$," G. K. Barker, M. Green, F. G. A. Stone, A. J. Welch, T. P. Onak, and G. Siwapanyoyos, *J. Chem. Soc.*, *Dalton Trans.*, 1687 (1979).

"Lower Rotational Barriers in Seven-Vertex than in Twelve-Vertex Carbaplatinaboranes: Synthesis and Molecular and Crystal Structures of $[closo-1,1-(Et_3P)_2-2,3-Me_2-1,2,3-PtC_2B_4H_4]$ and $[closo-1,1-(Et_3P)_2-1,2,4-PtC_2B_4H_6]$, G. K. Barker, M. Green, F. G. A. Stone, and A. J. Welch, *J. Chem. Soc.*, *Dalton Trans.*, 1186 (1980).

"Stepwise Formation of Di- and Tri-platinum Complexes with Bridging Alkyne Ligands; Crystal Structure of $[Pt_3\{\mu-(\eta^2-PhC_2Ph)\}_2(PEt_3)_4]$," N. M. Boag, M. Green, J. A. K. Howard, J. L. Spencer, R. F. D. Stansfield, M. D. O. Thomas, F. G. A. Stone, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 2182 (1980).

"Platinum-Osmium Carbonyl Complexes Derived from Di-μ-hydridodecacarbonyltriosmium; X-ray Crystal Structure of $[Os_3Pt(\mu-H)_2(CO)_{10}\{P(cyclo-C_6H_{11})_3\}]$," L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 155 (1981).

"Some Reactions of the Platinumtriosmium Complexes $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PR_3)]$ with Donor Molecules; X-Ray Crystal Structures of $[Os_3Pt(\mu\text{-}H)_2(CO)_{10}(PPh_3)_2]$ and $[OsPt_2(CO)_5(PPh_3)_2(\mu_3\text{-}MeC_2Me)]$," L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 162 (1981).

"Synthesis and X-ray Crystral Structure of $[NiOs_3(\mu\text{-}H)_2(\bar{\mu}\text{-}CO)_2(CO)_8(PPh_3)_2]$ and $[Os_3Rh(\mu\text{-}H)_2(acac)(CO)_{10}]$ (acac = acetylacetonate)," L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, 171 (1981).

"Synthesis and X-Ray Crystal Structure of $[N(PPh_3)_2][Fe_2Pt_2(\mu\text{-}H)(\mu\text{-}CO)_3(CO)_5(PPh_3)_2]$, $[Fe_2Pt_2(\mu\text{-}H)_2(CO)_8(PPh_3)_2]$ and $[Fe_2Pt(cyclo\text{-}C_8H_{12})(CO)_8]$," L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, F. G. A. Stone, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, in press (1981).

"Diosmium-Diplatinum Carbonyl Complexes Derived from Dihydridotetracarbonlylosmium; X-Ray Crystal Structure of $[Os_2Pt_2(\mu\text{-}H)_2(\bar{C}O)_8(PPh_3)_2]$," L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, and F. G. A. Stone, *J. Chem. Soc.*, *Dalton Trans.*, in press (1981).

"Dimolybdenum Complexes Derived from Cyclo-octatetraene: Crystal and Molecular Structures of $[Mo_2(CO)_2(\eta\text{-}C_5H_5)_2(C_8H_8)]$ (Two Isomers) and of $[Mo_2(CO)_4(\eta\text{-}C_5H_5)_2(\eta^3, \eta'^3\text{-}C_{16}H_{16})]$," R. Goddard, S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, in press (1981).

"Dimolybdenum Complexes Derived from Cyclo-octa-1,5-diene and Penta-1,3-Diene: Crystal and Molecular Structure of $[Mo_2(CO)_3(\mu\text{-}C_8H_{10})(\eta\text{-}C_5H_5)_2]$," S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, in press (1981).

"Reactions of Cyclic-1,3-Dienes with Ethyne Coordinated at a Dimetal Centre; Crystal Structure of $[Mo_2(CO)_2(\mu\text{-}\eta^2, \eta'^2\text{-}C_{10}H_{10})(\eta\text{-}C_5H_5)_2]$," S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, and P. Woodward, *J. Chem. Soc.*, *Dalton Trans.*, in press (1981).

"Synthesis of New Inorganic and Organometallic Materials," F. G. A. Stone, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The object of this work was to synthesize and to structurally characterize new organometallic compounds which are potentially useful materials. Specific areas for study were: (1) Polynuclear metal structures involving atoms of different elements. This aspect of the work was to include extension of earlier researches on platinacarbaboranes. (2) The activation of acetylenes and olefins by metal complexes, and (3) New chemistry of fluorocarbon complexes of transition metals. Research was carried out in all three areas, but as the project developed emphasis was placed on topics (1) and (2) in view of their increasing interest to chemists.

During the period of this grant several significant discoveries were made in the area of organometallic chemistry. Among the more important results were the following:

(A) New synthetic methods for obtaining polynuclear metal compounds with heteronuclear metal - metal bonds, e.g., species with Os - Pt, Os - Ni, Os - Rh, and Fe - Pt bonds.

(B) Oxidative addition of Pt^0 compounds to nido carbaboranes to give nido cage compounds which on subsequent pyrolysis afford closo-platninacarbaboranes.

(C) The discovery of the first metal cluster compound with a planar cyclo-octa-tetraene ring coordinated to three nickel atoms.

(D) Experimental demonstration of the high reactivity of the dimolybdenum complex $[Mo_2(CO)_4(n\text{-}C_5H_5)_2]$ towards cyclo-octa-tetraene, cyclo-octa-1,5-diene, and other dienes. This work has pointed the way to new chemistry at dimetal centers.

(E) The discovery of di- and tri-platinum complexes with bridging acetylene ligands; in particular the step-wise synthesis of these compounds from monoplatinum acetylene compounds.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Analytical Approach to the Selection of the Reaction Coordinate in the Calculation of Reaction Profiles

2. PRINCIPAL INVESTIGATOR: Professor Almon G. Turner
Department of Chemistry
University of Detroit
4001 W. McNichols Road
Detroit, MI 48221

3. INCLUSIVE DATES: 15 May 1981 - 15 July 1981

4. GRANT NUMBER: AFOSR-81-0114

5. COSTS AND FY SOURCE: $10,000, FY81 (MINI GRANT)

6. PUBLICATIONS:

"Analytical Approach to the Selection of the Reaction Coordinate in the Calculation of Reaction Profiles," Almon G. Turner, Final Technical Report.

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

An algebraic method for the analytical determination of an expression for the reaction coordinate in an arbitrary potential energy surface was presented. The method was applied to the thionyl imide - thiazyl S hydroxide isomerization reaction. The extent to which the method leads only to required reaction coordinate was dependent upon the manner in which the potential energy surface was sampled to obtain input data for the calculations. Questions concerned with the effects of overcompleteness and undercompleteness of the basis set were considered. The effects of the choice of norm for the reaction coordinate was also investigated.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Structural and Dynamic Studies of Materials Possessing High Energy Content

2. PRINCIPAL INVESTIGATOR: Professor Nicholas J. Turro
Department of Chemistry
Columbia University
New York, New York 10027

3. INCLUSIVE DATES: 1 November 1977 - 31 October 1980

4. GRANT NUMBER: AFOSR-78-3502

5. COSTS AND FY SOURCE: $65,000, FY77; $65,395, FY78; $110,750, FY79

6. SENIOR RESEARCH PERSONNEL:

Dr. W. Cherry	Dr. J. Butcher
Dr. G. Gabor	Dr. Y. Tanimoto
Dr. N. Harrit	Dr. M. Aikawa
Dr. V. Ramamurthy	Dr. M. F. Mirbach
Dr. A. Yekta	Dr. M. J. Mirbach

7. JUNIOR RESEARCH PERSONNEL:

M.-F. Chow	S. Kanfer
G. Hefferon	J.-M. Liu

8. PUBLICATIONS:

"Solvent Sensitivity of Type II Photoreactions of Ketones as a Device to Probe Solute Location in Micelles," N. J. Turro, K.C. Liu and M.-F. Chow, Photochem. Photobio., 26, 413 (1977).

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"A Practical Synthesis of Semibullvalene," N. J. Turro, J.-M. Liu, H. E. Zimmerman, and R. E. Factor, J. Org. Chem., in press.

"The Impact of Magnetic Fields and Magnetic Isotopes on Organic Reactions Involving Radical Pairs and Diradicals," N. J. Turro, Pure Applied Chem., in press.

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9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A major goal of the research supported by this grant was the advancement of our knowledge of the nature and behavior of molecules possessing an exceptionally high energy content. Both triplet (ground state) molecular oxygen, $^3O_2$, and singlet (excited state) molecular oxygen, $^1O_2$, were studied. We employed product analysis, structure-reactivity relationships, chemiluminescence methods, and laser flash spectroscopy to assist in the establishment of mechanisms that provided an understanding of these oxidations. We extended our chemiluminescent methods to include pulsed generation of chemiluminescent species. For example, we examined potential precursors for the pulsed laser excitation of $^1O_2$. We also concluded a series of investigations of the generation and reactions of $^1O_2$ in polymer films. We are extending these studies to include oxidations on selected surfaces such as porous glass and silica. Finally, we discovered that applied laboratory magnetic fields can significantly influence reactions which generate $^1O_2$. We are now investigating whether the reactions of $^1O_2$ are significantly influenced by a magnetic field.

AFOSR Program Manager: Dr. Anthony J. Matuszko

COMPLETED PROJECT SUMMARY

1. TITLE: Applied Quantum Chemistry of Nonmetallic Materials

2. PRINCIPAL INVESTIGATOR: Professor John Van Wazer
Department of Chemistry
Vanderbilt University
Nashville, TN 37235

3. INCLUSIVE DATES: 1 November 1976 - 28 February 1981

4. GRANT NUMBER: AFOSR-77-3145

5. COSTS AND FY SOURCE: \$40,955, FY77; \$44,446, FY78; \$49,174, FY79; \$60,000, FY80

6. SENIOR RESEARCH PERSONNEL:

Dr. C. S. Ewig	Dr. S. N. Datta
Dr. R. Osman	Dr. B. S. Sudhindra

7. JUNIOR RESEARCH PERSONNEL: A. Sur

8. PUBLICATIONS:

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"Symmetries of Transition States in Isoenergetic Reactions," C. S. Ewig (in preparation).

"Applied Quantum Chemistry of Nonmetallic Materials," J. Van Wazer and C. Ewig, Final Technical Report.

9. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Research under this grant has developed new theoretical and computational methods for studying the properties of materials. In particular, it has addressed the problems of using ab initio computations to predict (a) chemical bonding in systems composed of heavy elements, (b) relativistic effects in molecules, and (c) core-electron spectra, such as obtained by XPS experiments, in heavy atoms and molecules. Practical computational techniques have been formulated and tested which allow not only improved understanding of the theory of materials, but also routine calculations of energies and structures of a variety of atomic and molecular systems.

The research carried out under the grant examined some of the most basic principles governing the ways in which materials are composed in terms of atoms and molecules. Our first objective was to pursue the concept of core electrons, whih are of comparatively high energy and do not participate directly in bonding between atoms, as opposed to the lower-energy valence electrons that do tend to form bonds. This distinction allows extremely efficient ab initio computational methods for the calculation of molecular structure, such as the NOCOR procedure we developed during the previous grant period. For example, we have shown that an increase in computational efficiency of roughly an order of magnitude for molecules composed of elements from successive rows of the Periodic Table may result.

Our original method was largely limited to nonrelativistic single-configuration calculations using simple basis sets to describe the electron distributions. This was found to be a surprisingly accurate way of describing relatively large molecular systems composed of moderately heavy elements, such as phosphorus, silicon and germanium. However during the present grant period we have extended both the theory and computer programs to make the procedure much more general. Thus it is now applicable to any set of basis functions, either single- or multiconfiguration calculations, species with unpaired electrons, and has the facility to treat relativistic effects, which predominate in many properties of heavy elements such as lead and uranium. Thus we have now developed a computational tool for predicting a variety of spectroscopic and chemical properties.

A number of discoveries in related fields was an outgrowth of this effort. From a theoretical viewpoint, by far the most significant was the development of the first completely relativistic theory of molecular structure, along with the associated computer programs. For this we have employed the self-consistent-field approach using the Dirac (relativistic) equation of electron motion. Implementation of the Dirac equation involved considerable computational complexity, since all orbitals are four-component complex functions instead of one-component real functions as in the nonrelativistic approximation. Although our program is presently at a level only analogous to the restricted Hartree-Fock method, we believe it may well provide a cornerstone of subsequent work in other laboratories on the theoretical chemistry of heavy elements. Relativistic effects are now known to be quite significant in determining the chemical properties of elements from the fifth and lower rows of the Periodic Table. For example, the (relativistic) spin-orbit energies of lead compounds are often greater than their bond energies. Therefore an ab initio technique for predicting such effects is of central importance to work in this field.

Another outgrowth of our study of core electron properties and relativistic corrections was a procedure for calculating high-energy ionization spectra, such as X-ray photoelectron spectra (XPS), of atoms. This type of spectroscopy measures the minimal energy required to remove an electron from a core orbital. We found that, employing previously-developed Dirac-Fock techniques for atoms, a striking agreement with the available experimental results could be attained. For example, differences between theory and experiment are often only 3% of the lowest errors previously reported - an error which approaches the experimental linewidth. We have now found this agreement to be consistent for core electrons with experimentally accessible energies throughout the Periodic Table.

AFOSR Program Manager: Dr. Anthony J. Matuszko

ATMOSPHERIC SCIENCES

Lieutenant Colonel Ted S. Cress

As the "single manager" for the Air Force basic research program, AFOSR supports atmospheric research both in-house at AF laboratories and through an extramural research program. While AFOSR maintains an active extramural program, the basic research program is dominated by the total in-house and contractual program at the Air Force Geophysics Laboratory (AFGL). In contrast to the AFGL basic research goals which support, more directly, the exploratory development efforts at the laboratory, the AFOSR sponsored extramural program is more widely ranging, looking towards the creation of the knowledge base that will serve problem solving efforts in the 10-15 year time frame. Close coordination between efforts at AFOSR and AFGL is observed to insure complementary programs and avoidance of duplicative efforts.

The purpose of the AFOSR atmospheric sciences basic research program is to stimulate and support innovative research that will ultimately lead to a more thorough understanding of physical processes of the atmosphere. The range and scope address temporally and spacially variable features across the spectrum of scales from molecular to global, from the earth's surface to the atmosphere's outer limits where solar variability is key. This domain includes nearly all geophysical processes influencing the use and performance of current and proposed Air Force ground-based and airborne systems. Effects on space-based systems are generally covered by other AFOSR program areas. Magnetospheric processes, on the other hand, are occasionally addressed within this program where ionospheric behavior must be understood.

The Atmospheric Sciences program is structured into two classical research areas; meteorology, and upper atmosphere structure and dynamics. Within these general categories areas of emphasis are imbedded and enjoy the greater share of available funding. In FY 81, as in FY 80, the program emphasized three areas; mesoscale meteorology, cloud physics, and atmospheric dynamics. In the upper atmosphere, efforts were focused on the global character of auroral zone variability and the latitudinal morphology of electron density irregularities at northern latitudes.

The goal of this short descriptive effort will be to address the major research areas, describe recent developments, emphasize foci of interest, and speculate on the future course of the sponsored program. The philosophy of concentration of effort in the research program will be apparent in this description. It is hoped this philosophy will avoid a "scatter-gun" approach and will lead to major new advances beyond that which would be produced by research efforts proceeding in "splendid isolation." The most rapid advance of scientific knowledge and understanding hinges on communication and the existence of a "critical mass." We strive for both.

Meteorology

The current program in meteorology is reflective of deliberate focussing. Mesoscale dynamics is the core effort of the current program; interdependent processes such as convection, radiation, and energy exchange with the planetary boundary layer (PBL) are key sub interests. Two related fields of research round out the current emphasis research areas; these include cloud physics and an exciting new capability to study vertical coupling and energy exchange processes - VHF radar. As a general statement these topic areas will remain areas of concern and emphasis for the foreseeable future.

Other areas of potential interest are many, but several of the more critical areas are aerosol physics, optical/IR transmission characteristics of clouds (i.e., the morphology of the hydrometeor populations), and the dynamics of the planetary boundary layer.

In the area of mesoscale meteorology, the efforts of Dr. Anthes and Dr. Carlson at the Pennsylvania State University have resulted in showing that basically synoptic scale data can be used in adequately engineered fine-mesh numerical models to generate and maintain mesoscale features smaller than the original data distribution. Further improvement is anticipated with improved surface and boundary-layer physics as well as fine scale observations. During FY 81 Dr. Peter Hobbs initiated an effort to investigate the role of the planetary boundary layer in the morphology of features of synoptic scale systems.

In cloud physics, the center of activity continues to be the tri-service sponsored effort by Dr. Kassner, University of Missouri-Rolla, to build a cloud simulation chamber of unsurpassed capability. At the current time the so-called "ROMULUS" chamber is being assembled and is anticipated to be operational in January 1984. It is anticipated that the future cloud physics program will revolve about the capabilities of this chamber for cloud, aerosol and optical physics research. Aerosol physics, in particular, remains a critical area of interest. We understand little of discrete particle composition and refractive index; size distribution measurements are rendered suspect by ambiguities introduced by relative humidity effects and pulse analysis electronics. These will remain topics of interest for some time.

In studying vertical coupling and vertical energy transport, the mesospheric-tropospheric-stratospheric (MST) VHF radar developed by NOAA continues as an exciting new research tool. AFOSR is continuing to sponsor several studies of lower atmospheric dynamics with this facility and in the future may sponsor further investigations of vertical dynamic coupling. This radar's utility for synoptic or mesoscale research is intriguing and its potential for operational application is promising. Support to conduct quantitative investigations of atmospheric synoptic features is likely.

Upper Atmosphere

The upper atmospheric research program is focussed on understanding the temporal and spacial morphology of ionospheric structure (specifically electron density irregularities and gradient) and the dynamics of upper atmosphere motion. These questions are global in nature and impact numerous research activities such as auroral zone phenomenology, equatorial F-region irregularities, neutral winds, chemical species distribution, solar impacts on the neutral atmosphere, temporal and spacial ionospheric disturbances, inadvertent and planned ionospheric modification and ionospheric-magnetospheric coupling (modeling).

As in meteorology, the upper atmospheric research program is focussed. Current funding addresses the 2-D spacial and temporal variability of the auroral zone ionosphere and the latitudinal morphology of electron density irregularities at high latitudes. Smaller efforts address the spectrum of scintillation causing electron density irregularities and the role of neutral atmospheric processes in the global distribution of model (10-100 km) atmospheric trace species.

By far, the current program is dominated by the effort of SRI (Dr. Odile de la Beaujardiere) and MIT (Dr John Evans) to use simultaneous data from three incoherent scatter radars (Chatanika, Alaska; Millstone Hill, MA; and Tromso, Norway) to investigate auroral zone and subauroral zone dynamics and morphology. In cooperation NASA is providing Dynamic Explorer data which will permit the quantitative data of the radars to be extrapolated from the satellite imagery to the auroral zone between the radar sites. New understanding of temporally and spacially variable features should result from this effort. Results will be especially valuable to theoretical modelers. All in all this effort appears to be the right program at the right time - about six major research groups are currently involved with additional funding support from their own countries, NSF or ONR, permitting their participation. In a data acquisition phase to 1 March 1982, this effort is becoming all analytical in FY 82.

Support will continue in the upper atmospheric research program for viable research efforts that will lead to increased understanding of neutral and nonneutral atmospheric dynamics and an appreciation for potential problems and risks as we continually evolve new dependencies upon upper atmospheric processes.

COMPLETED PROJECT SUMMARY

1. TITLE: The Morphology of Stratospheric Planetary Waves

2. PRINCIPAL INVESTIGATOR: Dr. Arthur D. Belmont
Meteorology Department
Research Division
Control Data Corporation
Minneapolis, MN 55440

3. INCLUSIVE DATES: 1 January 1978 - 31 May 1981

4. CONTRACT NUMBERS: F49620-78-C-0036; F49620-79-C-0160

5. COSTS AND FY SOURCE: $37,000, FY78; $28,800, FY79; $50,700, FY80
$34,300, FY81

6. SENIOR RESEARCH PERSONNEL:

D. G. Dartt
R. W. Wilcox

7. PUBLICATIONS AND PRESENTATIONS:

"The Morphology of Stratospheric Planetary Waves, 10 to 0.4 mb," D. G. Dartt, R. W. Wilcox, and A. D. Belmont, Interim Report, AFOSR Contract F49620-79-C-0160 (1980).

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"The Morphology of Stratospheric Planetary Waves," D. G. Dartt, R. W. Wilcox, and A. D. Belmont, Final Report, AFOSR Contract F49620-70-C-0160 (1981).

"Diagnosis of Seven Stratospheric Sudden Warmings Using Wave Parameters from 850 to 0.4 mb, 1970-1974," D. G. Dartt, submitted to Mon. Wea. Rev., (1982).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research involved study of planetary waves in the stratosphere based on global temperature and geopotential height data derived from satellite measurements of atmospheric radiance. The measurements were obtained from the polar-orbiting Nimbus 4 and Nimbus 5 between 1970 and 1974. The computations resulted in daily time series of planetary wave coefficients of height and temperature which were used in a global analysis of the behavior of the major temperature waves. The first phase of the research examined four layers between 10 and 0.4 mb pressure (approximately 30 to 55 km altitude). Seasonal variations of the wave regimes and their relation to the zonal (east-west)

wind velocity were documented and a well-defined small-amplitude wave component was found in the upper stratosphere that had previously been detected only in the lower stratosphere. Coupling of wave motions across the equator was noted during certain time periods.

A second phase of the research centered on the relationship of planetary waves to the phenomenon of sudden stratospheric warming. This involved computation of wave parameters down to 850 mb (about 5 km). Seven stratospheric warmings during the observational period all corresponded to similar behavior of heat and momentum flux of wave number 1 and zonal mean values of temperature, vertical motion, and meridional (north-south) wind. This result leads to the suggestion that monitoring the wave heat flux and the zonally averaged winds from the surface to the upper stratosphere during the winter months would allow the prediction zonal heating during sudden warmings.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Low Level Convergence and the Prediction of Precipitation

2. PRINCIPAL INVESTIGATOR: Dr. Stanley A. Changnon, Jr.
Dr. Bernice Ackermann
Illinois State Water Survey
University of Illinois
P.O. Box 232
Urbana, IL 61801

3. INCLUSIVE DATES: 15 March 1979 - 30 September 1981

4. GRANT NUMBER: AFOSR-ISSA-79-0028 and AFOSR-ISSA-80-0029 (National Science Foundation Grant ATM-78-08865)

5. COSTS AND FY SOURCE: $35,000, FY79; $40,000, FY80

6. OTHER RESEARCH PERSONNEL:

Dr. Michael Garstang, Univ of Va.
Dr. Ronald Holle, ERL-NOAA

7. PUBLICATIONS:

"Low Level Convergence and the Production of Convective Precipitation," First Progress Report, Illinois State Water Survey, 15 Feb 1979.

"METROMEX Revisited," B. Ackerman, Preprints, Seventh Conf. on Inadvertent and Planned Wea. Mod., Oct 8-12, 1979, Banff, Amer. Meteor. Soc., Boston, 26-27 (1979)

"Morphology of Seeded Clouds as Determined from Triple-Doppler Radar - A Case Study," J. B. Cunning, R. I. Sax, and R. L. Holle, Preprints, Seventh Conf. on Inadvertent and Planned Wea Mod., Oct 8-12, 1979, Banff, Amer. Meteor. Soc., Boston, 142-143 (1979).

"Low Level Convergence and the Production of Convective Precipitation, Second Progress Report," Illinois State Water Survey, 2 January 1980.

"The Morphology of Isolated Severe Rainstorms and Hydroclimatological Characteristics of Such Storms," S. A. Changnon, Jr., and J. L. Vogel, Preprints, Second Conf. on Flash Floods, Atlanta, March 18-20, 1980., Amer. Meteor. Soc., Boston (1980).

"Outflow from a Nocturnal Thunderstorm," R. W. Scott, Illinois State Water Survey Contract Report 242 (1980).

"Boundary Layer Structure and Its Relation to Precipitation over the St. Louis Area," G. L. Achtemeier, Illinois State Water Survey Contract Report 241 (1980).

"Diurnal Interaction between Convection and Peninsula-Scale Forcing over South Florida," M. J. Cooper, M. Garstang, and J. Simpson, submitted to Mon. Wea. Rev.

"The Role of Near Surface Outflow in Maintaining Convective Activity," Proc. IAMAP, Hamburg (1981).

"Low-level Convergence and the Prediction of Convective Precipitation in South Florida," A. I. Watson, R. L. Holle, J. B. Cunning, P. T. Gannon, and D. O. Blanchard, Technical Report 4, NSF Grant ATM 78-08865 (1981).

"The Behavior of Surface Wind and Thermodynamic Fields with Presence of Deep Convection," H. J. Cooper and M. Garstang, Technical Report 5, NSF Grant ATM 78-08865 (1981).

"The Effect of Spatial Variability in Precipitation on Streamflow," K. J. Beven and G. M. Hornberger, Technical Report 6, NSF Grant ATM 78-08865 (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

In order to increase the understanding of the dynamics involved in the initiation of convective clouds, cloud interactions with mesoscale dynamics, and the initiation of precipitation, the Illinois State Water Survey (ISWS), the University of Virginia (UVA), and NOAA/NHEML collaboratively, and with funding from AFOSR, NSF and ARO, initiated an extensive effort encompassing existing data from METROMEX and the Florida Area Cumulus Experiment (FACE), as well as a major field program in central Illinois. ISWS concentrated their efforts on the cell and cloud scale while UVA studied the intermediate cloud and rain system scale, and NOAA investigated Mesoscale flow and divergence patterns in the boundary layer.

Initial studies of METROMEX and FACE data have indicated a correlation between subcloud divergence patterns and precipitation development with a measurable convergence preceding precipitation by up to several hours. This finding was found common to FACE and to convective scale flow patterns in Illinois. Correlating mid-level moisture fields and precipitation revealed a factor of 2-3 increase in precipitation from convective systems developing in the presence of middle level moisture versus similar development on "drier" days.

In the Illinois field experiment radar studies showed that convective clouds, in quasi-organized but nonfrontal convective activity, were characterized by a persistent cellular structure. Surprisingly no individual cells were found to produce excessive rainfall; only when cloud motion and cellular pattern caused successive cells to affect the same ground site was excessive precipitation experienced.

Further analysis of the data base developed in this program may continue under NSF funding. It is anticipated that the range of activity will encompass the effect of distant convective development on local convective dynamics, the upward and downward transport induced by divergence fields (dry days apparently are characterized by more upward transport than downward and on wet days the exchange is more even), convergence induced by convective outflow, and further clarification of the relationships between divergence field patterns and subsequent rainfall patterns. Modeling will become much more important as many relationships become better understood.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Structure of the Upper Atmosphere

2. PRINCIPAL INVESTIGATOR: Dr. Jeffrey M. Forbes
Department of Physics
Boston College
Chestnut Hill, MA 02167

3. INCLUSIVE DATES: 1 January 1977 - 31 December 1980

4. GRANT NUMBER: AFOSR-77-3223

5. COSTS AND FY SOURCE: \$30,000, FY77; \$21,788, FY78; \$22,365, FY79; \$20,647, FY80

6. JUNIOR RESEARCH PERSONNEL:

M. E. Hagan
C. Foley

7. PUBLICATIONS:

"Seasonal-Latitudinal Structure of the Diurnal Thermospheric Tide, J. M. Forbes and H. B. Garrett, J. Atmos. Sci., 35, 148-159 (1978).

"Tidal Structure of the Thermosphere at Equinox," H. B. Garrett and J. M. Forbes, J. Atmos. Terr. Phys., 40, 657-668 (1978).

"Tidal Variations in Thermospheric O, O_2, N_2, Ar, He, and H," J. M. Forbes, J. Geophys. Res., 83, 3691-3698 (1978).

"Solar Tidal Wind Structures and the E-Region Dynamo, J. M. Forbes and H. B. Garrett, J. Geomag. Geoelec., 31, 173-182 (1979).

"Tides in the Joint Presence of Friction and Rotation: An f-plane Approximation," J. M. Forbes and M. E. Hagan, J. Geophys. Res., 84, 803-810 (1979).

"Tidal Dynamics and Composition Variations in the Thermosphere," J. M. Forbes and M. E. Hagan, J. Geophys. Res., 85, 3401-3406 (1980).

"Seasonal-Latitudinal Tidal Structures of O, N_2, and Total Mass Density in the Thermosphere," J. M. Forbes and F. A. Marcos, J. Geophys. Res., 85, 3489-3493 (1980).

"Theoretical Studies of Atmospheric Tides," J. M. Forbes and H. B. Garrett, Rev. Geophys. Space Phys., 17, 1951-1981 (1979)

"Mesospheric and Thermospheric Tides," J. M. Forbes, J. Meteorol. Soc. Japan, 58, 298-301 (1980).

"Tidal Effects on D and E Region Ion Chemistries," J. M. Forbes, J. Geophys. Res. (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Initial efforts during the 4-year period of this grant involved investigations of the seasonal-latidudinal structure of the diurnal thermospheric tide and the thermospheric extensions of semidiurnal tides excited below 200 Km using a numerical model which realistically simulates dissipative processes. This work, combined with a calculation of the in-situ semidiurnal thermospheric tide, led to construction of a synthesized model of diurnal and semidiurnal temperatures and winds calibrated with incoherent scatter radar observations. This model was subsequently utilized to investigate tidal variations in thermospheric composition and the generation of electric fields and currents due to dynamo action in the E region (90-160 Km altitude). A rotating plane equivalent gravity wave formalism was also developed to more efficiently compute thermospheric tidal structures, and utilized to investigate the damping effect of O-N_2 mutual diffusion on thermospheric tides, and the mutual coupling between tides and turbulence in the mesosphere. Work under this grant formed an important contribution to a comprehensive review of theoretical studies of atmospheric tides written for Reviews of Geophysics and Space Physics in 1979. Finally, significant effects of tidal variations in temperature and density on the hydrated positive ion chemistry of the D region (70-90 Km) have been discovered, thus explaining some important aspects of the asymmetric and seasonal-latitudinal behavior of the D region.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Structure of the Upper Atmosphere

2. PRINCIPAL INVESTIGATOR: Dr. Jeffrey M. Forbes
Department of Physics
Boston College
Chestnut Hill, MA 02167

3. INCLUSIVE DATES: 1 January 1977 - 31 December 1980

4. GRANT NUMBER: AFOSR-77-3223

5. COSTS AND FY SOURCE: $30,000, FY77; $21,788, FY78; $22,365, FY79;
$20,647, FY80

6. JUNIOR RESEARCH PERSONNEL:

M. E. Hagan
C. Foley

7. PUBLICATIONS:

"Seasonal-Latitudinal Structure of the Diurnal Thermospheric Tide, J. M. Forbes and H. B. Garrett, J. Atmos. Sci., 35, 148-159 (1978).

"Tidal Structure of the Thermosphere at Equinox," H. B. Garrett and J. M. Forbes, J. Atmos. Terr. Phys., 40, 657-668 (1978).

"Tidal Variations in Thermospheric O, O_2, N_2, Ar, He, and H," J. M. Forbes, J. Geophys. Res., 83, 3691-3698 (1978).

"Solar Tidal Wind Structures and the E-Region Dynamo, J. M. Forbes and H. B. Garrett, J. Geomag. Geoelec., 31, 173-182 (1979).

"Tides in the Joint Presence of Friction and Rotation: An f-plane Approximation," J. M. Forbes and M. E. Hagan, J. Geophys. Res., 84, 803-810 (1979).

"Tidal Dynamics and Composition Variations in the Thermosphere," J. M. Forbes and M. E. Hagan, J. Geophys. Res., 85, 3401-3406 (1980).

"Seasonal-Latitudinal Tidal Structures of O, N_2, and Total Mass Density in the Thermosphere," J. M. Forbes and F. A. Marcos, J. Geophys. Res., 85, 3489-3493 (1980).

"Theoretical Studies of Atmospheric Tides," J. M. Forbes and H. B. Garrett, Rev. Geophys. Space Phys., 17, 1951-1981 (1979)

"Mesospheric and Thermospheric Tides," J. M. Forbes, J. Meteorol. Soc. Japan, 58, 298-301 (1980).

"Tidal Effects on D and E Region Ion Chemistries," J. M. Forbes, J. Geophys. Res. (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

Initial efforts during the 4-year period of this grant involved investigations of the seasonal-latidudinal structure of the diurnal thermospheric tide and the thermospheric extensions of semidiurnal tides excited below 200 Km using a numerical model which realistically simulates dissipative processes. This work, combined with a calculation of the in-situ semidiurnal thermospheric tide, led to construction of a synthesized model of diurnal and semidiurnal temperatures and winds calibrated with incoherent scatter radar observations. This model was subsequently utilized to investigate tidal variations in thermospheric composition and the generation of electric fields and currents due to dynamo action in the E region (90-160 Km altitude). A rotating plane equivalent gravity wave formalism was also developed to more efficiently compute thermospheric tidal structures, and utilized to investigate the damping effect of O-N_2 mutual diffusion on thermospheric tides, and the mutual coupling between tides and turbulence in the mesosphere. Work under this grant formed an important contribution to a comprehensive review of theoretical studies of atmospheric tides written for Reviews of Geophysics and Space Physics in 1979. Finally, significant effects of tidal variations in temperature and density on the hydrated positive ion chemistry of the D region (70-90 Km) have been discovered, thus explaining some important aspects of the asymmetric and seasonal-latitudinal behavior of the D region.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Geophysical Analysis of Coherent Satellite Scintillation Data

2. PRINCIPAL INVESTIGATOR: Dr. Edward J. Fremouw
Physical Dynamics, Inc.
P.O. Box 3027
Bellevue, WA 98009

3. INCLUSIVE DATES: 1 October 1977 - 30 September 1981

4. CONTRACT NUMBER: F49620-78-C-0014

5. COSTS AND FY SOURCE: $49,915, FY78; $50,000, FY79; $49,970, FY80; $62,634, FY81

6. JUNIOR RESEARCH PERSONNEL:

J. M. Lansinger
D. A. Miller

7. PUBLICATIONS AND PRESENTATIONS:

"Some Characteristics of Phase and Intensity Scintillation in Alaska, E. J. Fremouw and J. M. Lansinger, paper presented at National Radio Science Meeting (Spring URSI), University of Washington, Seattle, June 1979.

"On the Ratio of Intensity and Phase Scintillation Indices," E. J. Fremouw, paper presented at National Radio Science Meeting (Spring URSI), University of Washington, Seattle, June 1979.

"The Status of Scintillation Modeling," E. J. Fremouw, invited review paper presented at National Radio Science Meeting (Fall URSI), University of Colorado, Boulder, November 1979.

Contribution to "Transionospheric Propagation Predictions," E. J. Fremouw, compiled by J. Klobuchar in Solar-Terrestrial Predictions Proceedings, Vol. 2, ed. by R. F. Donnelly, Boulder, December 1979.

"Geometrical Control of the Ratio of Intensity and Phase Scintillation Indices," E. J. Fremouw, J. Atmos. Terr. Phys., 42, 775-782, 1980.

"On the Three-Dimensional Configuration of Scintillation-Producing Irregularities in the Auroral Zone," E. J. Fremouw and J. M. Lansinger, paper presented at 4th Scientific Assembly of IAGA, Edinburgh University, August 1981.

"Dominant Configurations of Scintillation-Producing Irregularities in the Auroral Zone," E. J. Fremouw and J. M. Lansinger, J. Geophys. Res., 86 (All), 1981).

"Geophysical Analysis of Coherent Satellite Scintillation Data," E. J. Fremouw, J. M. Lansinger, and D. A. Miller, Final Report, Contract F49620-78-C-0014 (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research was designed to extend knowledge of the occurrence, strength, and shape of ionospheric irregularities that produce radio wave scintillation in the auroral and sub-auroral latitudes. Signal phase and amplitude data from the Defense Nuclear Agency multi-frequency beacon on Air Force Satellite P76-5 were used to estimate shape parameters and to map out height-integrated irregularity strength. Data were recorded at VHF, UHF, and L-band from mid-1976 through 1978, although this project involved primarily the VHF phase data. Of particular interest were the identification of seasonal variations, effects of the solar activity cycle, and relationship to other high-latitude geophysical phenomena. The research also included a critical evaluation of the analysis methods used in this and related work, which led to reprocessing some of the data and raised questions concerning the short-term quantitative value of single-receiver measurements.

No statistically significant seasonal variation was found from these data, in the Alaskan sector, in sharp contrast to results obtained in the Greenland sector, but a quantitative relationship was found between phase scintillation and sunspot number and solar radio flux. Dominant spatial configurations of the irregularities were established, but difficulties were encountered in their quantitative description. The results suggest that large-scale sheetlike irregularities develop as a result of soft-electron precipitation into the ionospheric F-layer.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Analysis of Severe Weather Using Digital Doppler and Non-coherent Radar Data

2. PRINCIPAL INVESTIGATOR: Dr. George Huebner
Department of Meteorology
Texas A&M University
College Station, TX 77843

3. INCLUSIVE DATES: 1 December 1979 - 28 February 1981

4. GRANT NUMBER: AFOSR-80-0063

5. COSTS AND FY SOURCE: $7,000, FY80

6. JUNIOR RESEARCH PERSONNEL: D. J. McMorrow

7. PUBLICATIONS:

"Precipitation Field and Intrastorm Flow of Supercell Convective Storms," D. J. McMorrow, Texas A&M Univ., Final Report, Grant AFOSR-80-0063 (1981).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This investigation was the first detailed study of single-Doppler radar data in conjunction with surface rainfall data measured over short time intervals. Data from single Doppler radars were compared to those from multiple Doppler radars and to numerical simulations. These comparisons showed that features of the kinematic structure inferred from single Doppler radars could be reliably related to changes in precipitation rate at the surface.

A statistical relationship was found between point rainfall amounts and the areal coverage of rates greater than a specified threshold. It was determined that intrastorm kinematic flow could be estimated from data from a single Doppler radar with supplemental information about the environmental flow. The single Doppler radar has thus been shown to have a larger potential role in severe storm studies than simply monitoring tornadic and pretornadic wind velocity structures.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Experiments in Regional Scale Numerical Weather Prediction Including Use of SESAME '79 Data

2. PRINCIPAL INVESTIGATOR: Dr. Carl W. Kreitzberg
Department of Physics and Atmospheric Science
Drexel University
Philadelphia, PA 19104

3. INCLUSIVE DATES: 1 July 1979 - 30 June 1980

4. CONTRACT NUMBER: F49620-79-C-0208

5. COSTS AND FY SOURCE: $39,000, FY79; $51,000, FY80

6. PUBLICATIONS:

"A Numerical Case Study of the Squall Line of 6 May 1975," C. B. Chang, D. J. Perkey, and C. W. Kreitzberg, J. Atmos. Sci., 38, 1601-1615.

7 ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

A moist and dry fine-mesh (∿ 140 km) numerical model was evaluated using several simulations including the 6 May 1975 Omaha squall line. The moist fine-mesh simulation reproduced several observable features of the squall system and could be used to study other unobservable features. Differential thermal advection was responsible for the creation of potential instability. Low-level horizontal thermal advection contributed to pressure falls which, in turn, enhanced the convergence into the warm tongue. These processes initiated a band of convection. Results of the dry simulation suggested that the location and orientation of the initial low-level convergence was determined by dry mechanisms, that the convective latent heat release increased the rate of cyclonic-scale occlusion and that the occlusion process was followed by the dissipation of the convection.

In addition to the fine-mesh simulations, a meso-mesh (∿ 35 km) simulation was conducted. Because of the increased resolution, this simulation was able to reproduce the narrowing of the convective band from 400 to 100 km. This narrowing and intensification generated large values of low-level convergence and cyclonic vorticity. These processes produced a band of intense upward verticle velocity which, along with the convective transports of heat and moisture, stabilized the static energy profiles. Further evaluations to the performance of this model will be conducted under NSF and NOAA funding.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Propagation of Transient Signals through Nonlinear Ionized Media

2. PRINCIPAL INVESTIGATOR: Professor Robert E. McIntosh
Electrical and Computer Engineering
University of Massachusetts
Amherst, MA 01002

3. INCLUSIVE DATES: 30 September 1978 - 30 June 1981

4. GRANT NUMBER: AFOSR-78-3729

5. COSTS AND FY SOURCE: $52,612, FY78; $71,757, FY80

6. JUNIOR RESEARCH PERSONNEL:

A. Malaga	M. S. Kotfila
J. E. Sarna	A. D. Humason

7. PUBLICATIONS:

"Optimal Electromagnetic Pulse Radiators," J. E. Sarna and R. E. McIntosh, Univ of Mass. Eng. Tech. Rept. No. ECE-EP-79-2 (1979).

"Optimum Pulse Radiation by Planar Antennas," R. E. McIntosh and J. E. Sarna, USNC/URSI Commission B Meeting, Seattle, WA (1979).

"Analysis of HF Pulse Reflection from a Randomly Varying Ionosphere," A. Malaga and R. E. McIntosh, IEEE Trans. Antennas and Propag., AP-27, 508-516 (1979).

"Concurrent Microwave and Spectral Diagnostics of a Low-Density Argon Plasma," M. S. Kotfila and R. E. McIntosh, Univ. of Mass. Eng. Tech. Rept. No. ECE-EP-80-1 (1980).

"Time Dispersion of Electromagnetic Pulses by the Ionosphere," R. E. McIntosh and A. Malaga, Radio Sci., 15, 645-654 (1980).

"Time Spreading of Transient Pulses by the Ionosphere," R. E. McIntosh, USNC/URSI Meeting, Quebec (1980.

"Optical Emission from a Low-Density Argon Plasma," R. E. McIntosh and M. S. Kotfila, IEEE Trans. Plasma Sci., PS-9, 63-67 (1981).

"Measurement and Calculations of Doppler Shifted HF Waves Reflected from a Disturbed Ionosphere," A. D. Humason and R. E. McIntosh, Univ. of Mass. Eng. Tech. Rept. No. ECE-EP-81-2 (1981).

"Mathematical Modeling of Ionospheric HF Communication Channels," R. E. McIntosh, URSI XX General Assembly, Washington, DC (1981).

"Propagation of Transient Signals through Nonlinear Ionized Media," R. E. McIntosh, Final Rept., Grant AFOSR-78-3729 (1981).

"Frequency Dispersion in the Ionosphere: A Mini Review," R. E. McIntosh and A. Malaga, IEEE Trans. Antennas and Propag., AP-29, 970-972 (1981).

"Bounds on the Optimum Performance of Planar Antennas for Pulse Radiation," R. E. McIntosh and J. E. Sarna, IEEE Trans. Antennas and Propag., AP-30, May issue (1982).

8. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This research was based on laboratory test apparatus and a model of ionospheric propagation developed under a previous AFOSR grant (AFOSR-75-2763). Objectives under the more recent grant included theoretical and experimental research in the dynamics of various gases during breakdown in the presence of microwave radiation and the modeling and measurement of high-frequency (HF) signals propagating through the ionosphere. Subsequently, the objectives were broadened to include derivation of pulse fading rates and ionospheric turbulence data from Doppler spectrum measurements and an attempt to observe the effects of internal gravity waves on pulse propagation characteristics.

The electromagnetic pulse propagation model has shown that delay distortion, diffuse multipath, and frequency incoherence effects are small compared to the discrete multipath spread resulting from large-scale variations of the ionospheric electron number density. Thus, substantial pulse compression can be achieved, even when the state of the ionosphere is highly nondeterministic. Measurements on a high-frequency propagation link between Ottawa, Ontario, and Amherst, Massachusetts, provided data on frequency dispersion which agreed with earlier modeling work at the University of Massachusetts and elsewhere and served to illustrate the effects of traveling ionospheric disturbances (TID's) in modulating the frequency dispersion. Laboratory experiments with low-pressure RF-generated argon plasma provided a comparison of concurrent optical emission and electron density data which verified the steady-state corona model of a plasma under these conditions. A peripheral study resulting from the optimum pulse propagation research determined performance bounds of antennas designed to radiate extremely short duration electromagnetic pulses; these results should permit increased efficiency in antennas designed for this purpose.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Aerosol Profiles vs. Meteorological Conditions

2. PRINCIPAL INVESTIGATOR: Dr. Reinhold Reiter
Fraunhofer Institute for Atmospheric
Environmental Research
Kreuzeckbahnstrasse 19
Garmisch-Partenkirchen
Federal Republic of Germany

3. INCLUSIVE DATES: 1 March 1977 - 29 February 1980

4. GRANT NUMBER: AFOSR-77-3228

5. COSTS AND FY SOURCE: $25,600, FY77; $25,600, FY78; $25,600, FY79

6. JUNIOR RESEARCH PERSONNEL:

R. Sladkovic
W. Carnuth

6. PUBLICATIONS:

"Parameterization of the Vertical Profile of the Aerosol Constitution in the Lower Troposphere as a Function of Meteorological Conditions and Horizontal Extension," R. Reiter, R. Sladkovic, and W. Carnuth, Interim Report, Grant AFOSR-77-3228 (1979).

"Parameterization of the Vertical Profile of the Aerosol Constitution in the Lower Troposphere as a Function of Meteorological Conditions and Horizontal Extension," R. Reiter, R. Sladkovic, and W. Carnuth, Final Report, Grant AFOSR-77-3228 (1981).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The Fraunhofer Institute has recorded aerosol and meteorological data at three sites near Garmisch-Partenkirchen since 1970. Located at surface elevations of 940, 1780, and 3000 m, these sites provide an estimate of the vertical variation of the recorded parameters. Most of the aerosol size and number data have been derived by microscopic examination of impaction slides, although some have been obtained by optical size-distribution measuring instrumentation. In support of Air Force needs, an analysis effort was undertaken to relate the aerosol parameters to meteorological conditions, including diurnal and seasonal variations, stability and convection, humidity, precipitation, and wind structure. A related objective was to determine the degree of horizontal uniformity of the aerosol profile under various meteorological conditions and thus to estimate the degree to which the measurements at Garmisch-Partenkirchen were representative of aerosol conditions elsewhere as related to synoptically measured meteorological data. Concurrent radio soundings at the Institute and by the German Weather Service in Munich, 90 km distant, were compared to assess the degree of similarity of the low-level atmospheric structure.

The parameterization of the aerosol data according to season, air mass type, temperature and humidity, aerosol mass per unit volume, visibility range, and height dependence provides a climatological data base for estimating visibility and optical transmissivity from meteorological data in central Europe. The radiosonde intercomparison suggested that the aerosol conditions observed at Garmisch-Partenkirchen would possibly be valid for about a 200 km radius, in the absence of synoptic-scale disturbances.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Scattering by Nonspherical Particulates

2. PRINCIPAL INVESTIGATOR: Dr. Donald W. Schuerman
Space Astronomy Laboratory
State University of New York at Albany
now at: Space Astronomy Laboratory
University of Florida
1816 NW G Street
Gainesville, FL 32601

3. INCLUSIVE DATES: 1 November 1978 - 31 October 1980

4. CONTRACT NUMBER: AFOSR-MIPR-78-0016; 79-0011; 80-0015
(To ARO Contract DAAG 29-78-G-0024)

5. COSTS AND FY SOURCE: $30,000, FY78; $30,000, FY79; $30,000, FY80

6. JUNIOR RESEARCH PERSONNEL:

Ru T. Wang	Bo Å. S. Gustafson
Richard W. Schaefer	J. Mayo Greenberg

7. PUBLICATIONS:

"A Systematic Study of Light-Scattering: 1. Particle Shape," D. W. Schuerman, R. T. Wang, B. Gustafson, and R. Schaefer, submitted for publication in Appl. Opt.

Light Scattering by Irregularly Shaped Particles, D. W. Schuerman, Ed., Plenum Press, New York, 1980.

"The Microwave Analog Facility at SUNYA: Capabilities and Current Programs," D. W. Schuerman, in Light Scattering by Irregularly Shaped Particles, D. W. Schuerman, Ed., Plenum Press, New York, 1980.

"Extinction Signatures of Non-Spherical/Non-Isotropic Particles," R. T. Wang, in Light Scattering by Irregularly Shaped Particles, D. W. Schuerman, Ed., Plenum Press, New York, 1980.

"Calculations of the Light Scattered by Randomly Oriented Ensembles of Spheroids of Size Comparable to the Wavelength," R. W. Schaefer, Ph.D. thesis, State University of New York at Albany, 1980.

"Scattering by Ensembles of Small Particles: Experiment, Theory and Application," B. Å. S. Gustafson, Ph.D. thesis, University of Lund, Sweden, 1980. Also published in Reports from the Observatory of Lund, 17, 1980.

8 ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This investigation examined the effect of particle shape in light scattering by clouds of identical particles. The scattering and absorption of light by particles whose size is of the order of the wavelength can be predicted theoretically in only a few special cases: arbitrary spheres, infinite cylinders, and arbitrary spheroids. How well such idealizations correspond to scattering by ensembles of real-world particles can be determined only by a systematic investigation of the role of particle shape. For nonspherical particles, the question assumes an additional complexity because the final results require averaging over a distribution (assumed random) of all particle orientations.

The light scattered and absorbed by an ensemble of randomly oriented, identical particles for each of the 28 spheroids of revolution depicted in Figure 1 was either measured or completed. All particles had the same index of refraction, m = 1.61 - i 0.004, which is representative of silicates. Their shapes and sizes were selected and arranged so that: (1) each particle has an axis of rotation that is parallel to the heavy arrow shown in the upper right of the figure; (2) from left to right, the particles change from cylinders, to prolate spheroids, to spheres, to oblate spheroids, to disks; (3) the surface area of each row of particles is approximately conserved; and (4) the linear dimensions of each row change by about 25%.

The tools required to accomplish the tasks of calculation and measurement were developed under this contract. The theory of Asano and Yamamota allowed for a complex index of refraction and for averaging over particle orientations. More importantly, the Microwave Analog Facility at the State University of New York at Albany (now at the University of Florida) was upgraded and automated so that the scattering properties of any arbitrarily shaped particle could be measured and averaged over a uniform distribution of the particle's orientation. This is the first time that true "random averaging" was accomplished experimentally.

The microwave analog method exploits the fact that in the theory of light scattering all particle dimensions enter only in units of the wavelength of the radiation. Thus, the microwave analog of visible light scattering by submicron particles is microwave scattering by targets whose sizes are of the order of centimeters. Under this contract a target suspension system was designed and constructed where, along with the use of computer-controlled stepping motors, a harness of invisible (to the microwaves) nylon threads moved the target through a predetermined sequence of orientations. This arrangement permitted the first general experimental verification of the spheroid theory, the first measurements of the scattering due to randomly oriented disks and cylinders, and made possible the investigation of light scattering due to a cloud of particles of arbitrary shape.

The angular intensity of scattered radiation as a function of scattering angle is described by an "F" matrix which operates on the incident (zero subscripted) Stokes vector,

$$(I_\ell, I_r, U, V) = F\,(I_{\ell 0}, I_{r0}, U_0, V_0).$$

For an ensemble of randomly-oriented, axially-symmetric particles, F has the form

$$F = \frac{\lambda^2}{4\pi r^2}\begin{bmatrix} i_{22}(\theta) & i_{21}(\theta) & 0 & 0 \\ i_{12}(\theta) & i_{11}(\theta) & 0 & 0 \\ 0 & 0 & a_3(\theta) & b_2(\theta) \\ 0 & 0 & -b_2(\theta) & a_4(\theta) \end{bmatrix}$$

The quantities i_{22}, i_{11}, and i_{12} ($=i_{21}$) are sufficient to describe the scattering of unpolarized or linearly polarized radiation, and these functions can be determined using the microwave method. The extinction cross-section (C_{ext}) can also be measured in the microwave lab as described in Publication 4. For each of the 28 particles, the following quantities can be derived from i_{11}, i_{22}, i_{12}, and C_{ext}:

Degree of polarization:

$$P(\theta) = \frac{i_{11}(\theta) - i_{22}(\theta)}{i_{11}(\theta) + 2i_{12}(\theta) + i_{22}(\theta)}$$

Total scattering cross-section:

$$C_{sca} = \frac{\pi}{k^2}\int_0^\pi \left\{i_{11}(\theta) + 2i_{12}(\theta) + i_{22}(\theta)\right\} \sin\theta d\theta$$

Absorption cross-section:

$$C_{abs} = C_{ext} - C_{sca}$$

The asymmetry factor:

$$\overline{\cos\theta} = \frac{\pi}{k^2 C_{sca}}\int_0^\pi \left\{i_{11}(\theta) + 2i_{12}(\theta) + i_{22}(\theta)\right\} \cos\theta \sin\theta d\theta$$

Radiation pressure cross-section:

$$C_{pr} = C_{ext} - \overline{\cos\theta}\, C_{sca}$$

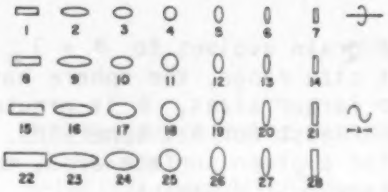

FIGURE 1

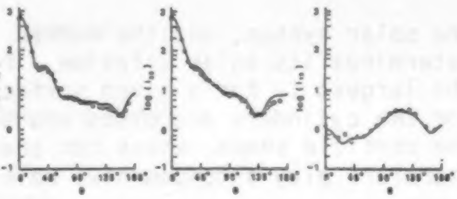

FIGURE 2

In Figure 2 a comparison between calculations (solid line and the "Computed" column of numbers) and measurements (dots and "Analog" column) for a large, 4:1, prolate spheroid (target number 24 of Figure 1) are displayed. Below are listed the most important findings of the role of particle shape, the sphere being used as a standard:

A. Angular Distribution of the Scattered Light. Scattering angles between 30^{0} and 45^{0} contain the least information on particle shape. The angular position of the absolute minimum intensities is always between $110^{0} < \theta < 160^{0}$ with only a slight rise toward $\theta = 180^{0}$ -- the spectacular rise in backscatter for spheres (the rainbow) is missing. The perpendicular component, $i_{11}(\theta)$, always has more angular variation than the parallel, $i_{22}(\theta)$, and the cross polarization, $i_{12}(\theta)$, is usually much smaller than the other components. In many cases, the maximum of i_{12} is nearly equal to the maximum of i_{11} or i_{22}.

B. Degree of Polarization. The degree of polarization as a function of scattering angle, $P(\theta)$, depends strongly on particle shape. It never exceeds ± 50%, whereas for spheres it may come close to -100% in this size range. For $\theta < 90^{0}$, the 4:1 prolate spheroids and 4:1 cylinders of the same surface area have nearly the same signatures in θ dependence, while the 2:1 prolate spheroids produces the reverse polarization. No such statement can be made for the oblate spheroids and disks. The degree of polarization, when averaged over $90^{0} < \theta < 180^{0}$, is more negative for the prolate particles than for the oblate. And for all shapes, including spheres, the oscillations in $P(\theta)$ increase with increasing size. Thus, $P(\theta)$ is an indicator of both the size and shape of the particle, and future studies should concentrate on delineating these relationships.

C. Extinction. The 4:1 prolate spheroids and 4:1 cylinders of the same surface area produce equivalent extinctions as do the three smallest 4:1 oblate spheroids and 4:1 disks. The extinction depends on the aspect ratio; the greater the aspect ratio, the larger the particle size at which the maximum extinction occurs. Most of the extinction results agree with the recent calculations of Asano and Sato (Appl. Opt., 19, 962-974, 1980) provided that one compares phase shift parameters rather than particle sizes.

D. Radiation Pressure Cross-Section. The quantity of interest here is β, the ratio of radiation to gravitational forces. This is an important astrophysical quantity because particles with $\beta > 1$ are purged from the interplanetary dust complex. This process is the ultimate sink of matter in the solar system, and the manner in which a dust grain evolves to $\beta = 1$ determines its solar lifetime. For the smallest size range, the sphere has the largest β for a given surface area; for the larger sizes, β is greatest for the cylinders and disks and surprisingly, the least for 4:1 spheroids. The particle shape, which can change β by 75% for a given surface area, may therefore play a fundamental role in interplanetary dust dynamics.

As an adjunct to this investigation, an "International Workshop on Scattering by Irregularly Shaped Particles" was held at Albany, New York, on 5-9 June 1979, whose proceedings are described in Publication 2.

AFOSR Program Manager: Ted S. Cress, Lt Col, USAF

COMPLETED PROJECT SUMMARY

1. TITLE: Atmospheric Absorption of Radiation by Water

2. PRINCIPAL INVESTIGATOR: Dr. Richard H. Tipping
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3. INCLUSIVE DATES: 1 February 1980 - 31 January 1981

4. GRANT NUMBER: AFOSR-80-0058

5. COSTS AND FY SOURCE: $9,990, FY80 (MINI GRANT)

6. PUBLICATIONS:

"The Dipole Autocorrelation Function for Molecular Pressure Broadening a Quantum Theory which Satisfies the Fluctuation-Dissipation Theorem," R. W. Davies, R. H. Tipping, and A. S. Clough, submitted to Physical Revue A (1981).

"Atmospheric Absorption of Radiation by Water," R. H. Tipping, Final Report, Grant AFOSR-80-0058 (1981).

7. ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

The research, conducted in collaboration with Air Force Geophysics Laboratory, focused on the modeling of water vapor absorption in the atmospheric "window" near 1000 cm^{-1} wavenumber (10 micrometer wavelength) where the so-called "continuum absorption" is not well understood in terms of either line structure or temperature dependence. This abosrption is thought to be due to the far wings of known absorption lines, but the effects of temperature and pressure on these far wings is not well known. Hence, the initial objective was to model individual abosrption spectral lines over their entire width and secondly to superpose the profiles of individual lines to yield a total absorption for a given wavenumber which would agree with experimental measurements of absorption as a function of temperature and pressure. The spectral line modeling effort was successful, and preliminary calculations of superposed spectral lines have yielded very encouraging results. Further research is contemplated (not necessarily under AFOSR sponsorship) to more fully compare the theoretical and experimental absorption values and also to examine the effects of molecular collisions in the continuum abosrption for wavenumbers below 1200 cm^{-1} (wavelengths above 8 micrometers).

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